RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XI NUMBER 4

October, 1938

Published under the Auspices of the
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

DUPONT
REG. U. S. PAT. OFF.

RUBBER CHEMICALS

• ACCELERATORS FOR EVERY PURPOSE

Zenite A*
Thionex*
Tetrone A*
D. O. T. G.
Formaniline
Accelerator No. 8*
Accelerator 808*
Accelerator 552*
Accelerator 122*

• OUTSTANDING ANTIOXIDANTS

Neozone A*
Neozone D*
Thermoflex A*
Antox*
Solux*

• SPECIAL RUBBER CHEMICALS

Barak*—Accelerator—Activator
RPA No. 2*—Rubber Peptizing Agent
Heliozone*—Sun Checking Resister
Retarder W*—Accelerator Inhibitor
Aquarex D*—Mold Lubricant and Latex Wetting Agent

• ATTRACTIVE COLORS FOR ALL RUBBER PRODUCTS

Rubber Dispersed Dry Powders
Pastes for Latex
Light fast—Brilliant—Economical

• NEOPRENE AND NEOPRENE LATEX

For Severe Service Involving
Oils—Heat—Ozone—Sunlight—Chemicals

Trade Mark exclusively owned and used by du Pont

FOR
BEST RUBBER PRODUCTS
Use DUPONT
RUBBER CHEMICALS

USE NEOPRENE
Where Other Materials Fail

•

Rubber Chemicals Division
E. I. DU PONT DE NEMOURS & COMPANY, INC.
WILMINGTON, DELAWARE

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor ..... C. C. Davis
Advertising Manager ..... S. G. Byam
Secretary ..... H. I. Cramer
Treasurer ..... C. W. Christensen

Vol. XI October, 1938 No. 4

CONTENTS

General Subjects

Page

Rubber Division Activities xxxix

New Books and Other Publications xl

Reprinted Papers

The Proteins in Preserved Hevea Latex. By C. Bondy and H. Freundlich. 601

The Creaming of Hevea Latex by Colloids. By C. F. Vester 608

Stability of Ficus Elastica Latex. By F. K. Daniel, H. Freundlich, and K. Söllner 624

A Colloidal and Chemical Investigation of Different Brands of Latex: Natural Latex, Jatex, Revertex, Revertex-T, and Revultex. By B. A. Dogadkin and B. M. Kovarskaya 630

The Kinetic Theory of the Elasticity of Rubber. By H. Pelzer 644

The Behavior of Raw Rubber when Stretched Isothermally. By H. Hintenberger and W. Neumann 647

The History of Rubber. Franz Carl Achard's "Experiments on Elastic Resin." By Leo Eck 653

The Fusion Curves of Rubber and Gutta-Percha. By Kurt H. Meyer 658

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the Act of August 24, 1912.

A New Transformation Product of Rubber. By O. Kratky, H. Philipp, K. W. Posnansky, and F. Schossberger..... 661

Colloidal Structure of Rubber in Solution. Effect of Precipitants. By S. D. Gehman and J. E. Field..... 663

Observations on the Viscosity of Rubber Solutions. By Eugene Guth.... 676

Chemistry of Soft Rubber Vulcanization. Reversion and Nonreversion in Low-Sulfur Compounds. By B. S. Garvey, Jr., and D. B. Forman..... 680

The Rubber-like Behavior of an Artificial Substance (Oppanol) when Irradiated with X-rays. By R. Brill and F. Halle..... 687

Determination of the Resistance of Vulcanized Rubber to Tearing. By D. J. van Wijk..... 689

Contributions to the Analysis of Rubber. III. Determination of Copper in Raw Rubber, in Mixtures, and in Fillers. By P. Dekker..... 706

Preparation and Testing of Latex Compounds. By J. W. MacKay..... 716

Oxygen Pressure Aging. Improved Equipment. By L. M. Freeman..... 722

Analysis of Organic Accelerators. By J. G. Robinson..... 728

Apparatus for Evaluating Puncture Resistance. By H. H. Bashore..... 740

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

To these charges of $2.00, $4.00, and $6.00, respectively, per year, extra postage must be added at the rate of $.20 per year for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

Chairman.....G. K. Hinshaw, The Goodyear Tire and Rubber Co., Akron, Ohio
Vice-Chairman.....E. B. Curtis, R. T. Vanderbuilt Co., 230 Park Ave., New York City
Secretary.....H. I. Cramer, University of Akron, Akron, Ohio
Treasurer.....C. W. Christensen, Monsanto Chemical Co., Akron, Ohio
Executive Committee.....A. R. Kemp, J. C. Walton, A. W. Carpenter, G. S. Haslam, W. G. Nelson, C. C. Davis, S. G. Byam
Sergeant-at-Arms.....E. H. Krismann

Acknowledgment

It is with great pleasure and appreciation that Rubber Chemistry and Technology announces the continuance of the financial assistance which the Rubber Manufacturers' Association has given so generously in the past.

The Rubber Manufacturers' Association has always realized the importance of Rubber Chemistry and Technology to the rubber industry, and has always responded most generously. The Rubber Division is therefore deeply indebted to the Association, and it is to be hoped that this support will be reflected in an increased proficiency of the technical staffs of the rubber companies, to the mutual advantage of all.

New Books and Other Publications

Rubber Statistics—1900–1937. Compiled by P. W. Barker. Bureau of Foreign & Domestic Commerce, Washington, D. C. 6 × 9 in. 10¢ per copy (for sale by Superintendent of Documents, Washington, D. C.).

For the first time, all the basic statistical data necessary to a study of the development of the rubber manufacturing industry from 1900 to 1937 have been made available. Production, absorption, stocks, and prices of crude rubber are covered, with data on prices going beyond 1900. Official annual and monthly trade returns of the countries producing or consuming rubber are the source of practically all of the statistics. The manner of presentation is: (1) short preliminary statement; (2) annual statistics, 1900 to 1937; (3) monthly statistics for the last twelve years. Only brief textual matter accompanies each major subdivision of the text, each table telling its own statistical story. The all-inclusive statistical booklet was prepared under the direction of E. G. Holt, acting Chief of the Leather and Rubber Division of the Bureau of Foreign & Domestic Commerce. [From *The Rubber Age* of New York.]

Rubber: Some Facts on Its History, Production & Manufacture. By P. W. Barker. Bureau of Foreign & Domestic Commerce, Washington, D. C. 8 × 10½ in. 36 pp. 5¢ per copy.

Furnishing general information on the production of rubber and the manufacture of rubber products, this pamphlet has been primarily prepared for school children, college students, and the general public. More attention has been given to the subject of rubber cultivation than to rubber manufacturing. The differences between wild and plantation rubber are stressed, with brief mention of reclaimed rubber and synthetic rubber. Some statistics are also given. [From *The Rubber Age* of New York.]

Rubber in Wegen. De Rubber Stichting, Heerengracht 182, Amsterdam, Holland.

This 34-page illustrated booklet was issued on the occasion of the Eighth International Road Congress and the Exhibition, "The Road in 1938." After an exposition of the work of the Rubber Stichting there are discussions of the technical properties of rubber, the use of rubber in road construction, and a list of experimental areas paved with rubber in different parts of the Netherlands. Altogether 17 such areas were laid; in 15 of these, combinations of asphalt emulsion and latex or of asphalt and crumb rubber, were used. Of the remaining two, one was laid with Gaisman blocks; while in the other, vulcanized rubber sheets were attached to the wooden surface of a bridge by means of wooden screws. [From the *India Rubber World.*]

The Effect of Rubber on Some Properties of Asphaltic Bitumen. By J. M. Van Rooijen. The Rubber Stichting, 182 Heerengracht, Amsterdam, Holland. 6¼ × 9½ in. 28 pp. (A limited number of copies available from *The Rubber Age.*)

Although changes which occur in the properties of asphaltic bitumen when rubber is added have been mentioned in the previous literature, no explanation has been offered as to why these changes take place. This booklet, a reprint of an article in a recent issue of *Materialenkennis*, contains such an explanation, and also brings

forward more factual material. Methods of estimating the properties of asphaltic bitumen-rubber mixtures are also given. This booklet is available in English, French, German, and Dutch. [From *The Rubber Age* of New York.]

Report of the Work of The Rubber Research Board (Ceylon) in 1937. London Advisory Committee for Rubber Research (Ceylon and Malaya), Imperial Institute, South Kensington, London, S. W. 7, England. 76 pp.

The seventh annual report for 1937 of the Rubber Research Scheme (Ceylon) contains individual reports by the following: Chairman, Director, Chemist, Botanist, and Mycologist, Smallholdings Propaganda Officer, Estate Superintendent, London Advisory Committee for Rubber Research (Ceylon and Malaya), and Auditor General. The technical appendix to the London committee's report included in this booklet contains information on: latex—specification and testing, preservation, concentration, and colloidal properties; rubber—softened rubber, "low water-absorption" rubber, synthetic rubber (Buna), and halogen derivatives of rubber from latex; road surfacing and flooring materials—latex-cement mixtures and rubber-asphalt mixtures. [From the *India Rubber World.*]

Symposium on Plastics. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. 51 pp.

This pamphlet comprises the six technical papers on plastics delivered at the society's regional meeting in Rochester, N. Y., March 9, 1938. These papers, many of them containing tabular data, and their authors, are as follows: "The Properties of an Ideal Plastic," A. F. Randolph; "A Discussion of Testing Methods for the Determination and Comparison of the Strength Properties of Various Organic Plastics," H. M. Richardson; "A Review of Methods for Measuring the Thermal Properties of Plastic Materials," W. A. Zinzow; "Flow Relations of Thermoplastic Materials," C. H. Penning and L. W. A. Meyer; "Hardness—as Applied to the Plastic Industry," J. C. Pitzer; "Permanence of Plastics," Gordon M. Kline. Copies of the pamphlet can be obtained from the society at 75¢ per copy. [From the *India Rubber World.*]

Photoelastic Determination of Stresses around a Circular Inclusion in Rubber. By W. E. Thibodeau and L. A. Wood. (A Reprint.) 6 × 9 in. 18 pp. For sale by the Superintendent of Documents, Washington, D. C. 5¢ per copy.

The possibilities of the use of rubber as a model material are indicated in this booklet, a reprint of an article from the March, 1938, issue of the *Journal of Research*, published by the National Bureau of Standards. The results of an analysis made of the stresses around a rigid circular inclusion with cemented boundary in a rubber sheet which is under simple tension at a distance from the inclusion, performed by the photoelastic method, are given. The authors found that the maximum stresses near the boundary of the disc are about 50 per cent greater than the average applied stress. [From *The Rubber Age* of New York.]

If I Only Had That Book. (Catalog No. 6.) Chemical Publishing Co. of N. Y., Inc., 148 Lafayette St., New York City. $5\frac{1}{2} \times 8\frac{1}{2}$ in. 150 pp. 10¢.

This latest catalog, like its predecessors, lists and describes chemical, bacteriological, pharmaceutical, medical, engineering, electrical, and general scientific and other technical books of American and British publishers. An index makes the location of any volume a simple matter. [From *The Rubber Age* of New York.]

The Text-Book Guide: 1938-39. Baker & Taylor Co., 55 Fifth Ave., New York City. 6 × 9 in. 156 pp.

As in previous editions, the 1938-39 guide not only lists the titles and authors of text-books covering a wide range of general and technical subjects, but carries factual descriptions of some of the more important books. [From *The Rubber Age* of New York.]

[Reprinted from the India-Rubber Journal, Vol. 95, No. 17, pages 513–516, April 23, 1938. The article appeared originally in the Comptes Rendus du Laboratoire de Carlsberg, Vol. 22.]

The Proteins in Preserved Hevea Latex

C. Bondy and H. Freundlich

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON

Hevea latex, the milky sap of *Hevea brasiliensis*, is a concentrated emulsion of rubber hydrocarbon in an aqueous solution which contains both colloidal and crystalloidal substances. Such concentrated emulsions are known to be stable only if a sufficient quantity of an emulsifying agent is present which, by coating the finely dispersed globules, prevents them from coalescing.[2] It has long been suggested that proteins, which are found in many latices, are adsorbed on the rubber particles and may, therefore, act as protective agents.[3] The importance of proteins for the colloidal behavior of *Hevea latex* was shown by a great number of experiments[4] which clearly proved that the latex had an isoelectric point so characteristic of protein coated surfaces, and furthermore, that this isoelectric point (i. p.) was identical with the i. p. of the mixture of proteins in the latex.[5] Further evidence for the important part played by proteins in the stability of latex was furnished by coagulation experiments,[6] showing that many typical protein precipitants were very efficient coagulants for latex.

The proteins of *Hevea latex* have been the subject of numerous investigations which were, however, mainly concerned with the influence of the nitrogenous substances on the manufacturing processes of rubber or the properties of the product ultimately obtained.[7] Although much work has been done regarding the coagulation of latex by modifying the protective protein layer around the rubber globules,[8] our knowledge of the proteins present in fresh or preserved *Hevea latex* still appears to be somewhat incomplete. With the exception of the extensive but mainly analytical work of Belgrave and Bishop[9] and a few papers by other authors,[10] no detailed account of the isolation and distinction of individual proteins of *Hevea latex* has come to the authors' attention. Our investigations, some results of which are communicated in this paper, were begun with the aim of filling this gap.

EXPERIMENTAL

A. The Preparation of the Serum

Ammonia-preserved *Hevea latex* (p_H 9.7) with a rubber content of 38 per cent[1] was centrifuged until the concentration of the "skim" was less than 6 to 7 per cent, this being achieved after about 20 hours. The centrifuge used had a mean diameter of 15 cm. and was running at a speed of 3000 r. p. m. The amount treated during one run was 800 cc., filled into four cups with a capacity of 220 cc. each. Little more than half the initial volume of liquid remained after the thick cream had been removed. The "skim" was then filtered through a porous pot of unglazed white china clay[11] with a capacity of 150 cc., as used in battery cells. The pot, soaked for two hours in boiling water, was fitted into a large filter flask by means of a rubber ring and filled with the liquid. The flask was then connected to an ordinary water pump. To facilitate filtration, the inner wall of the pot, on

which a thick deposit of rubber forms, was frequently rubbed with a rubber stopper on a glass rod. We thus obtained a clear, brownish serum without using any coagulants which had hitherto mostly been added. When studying proteins it is essential to avoid acids or alcohol, which may easily cause denaturation.

The total dry content of the serum was 3.4 per cent. The non-diffusible nitrogen amounted to 0.021 per cent which corresponds to a protein content of about 0.14 per cent.

B. The Isolation of the Proteins

1. *Protein A.*—The serum was adjusted to p_H 8 by neutralizing the excess of ammonia with dilute acetic acid. Into this solution half its own volume of a saturated ammonium sulfate solution was then stirred, the final p_H being 7.2. Voluminous flakes of a slightly brownish color separated, slowly rising to the top of the liquid. After about three hours, when the flakes began to settle, the precipitate was centrifuged off, resuspended in a 20-per cent ammonium sulfate solution, and centrifuged again. The protein was then redissolved in distilled water containing a trace of ammonia (it could not easily be dissolved in neutral solutions), and the operations of reprecipitation were repeated twice under analogous conditions. The protein thus purified and dissolved in dilute ammonia (p_H 8.5) was dialyzed in a cellophane bag for 24 hours against frequently renewed distilled water. A few drops of toluene were added as a bactericide. Thymol was found to be insufficient to prevent bacterial decay. The solution was then transferred into an electrodialyzer of the Pauli[12] type, and electrodialyzed until the current reached a constant value, usually about six hours, with a potential gradient of 45 volts per cm. During this time the current density fell from about 2 ma. per sq. cm. to 0.3 ma. per sq. cm. The membranes used were collodion at the cathode and collodion + gelatin, prepared according to Ettisch and Ewig,[13] at the anode. The p_H was constantly controlled, and, during the first two hours, kept on the alkaline side by adding minute amounts of ammonia. The hydrogen-ion concentration was then allowed to increase slowly until it reached the final value of p_H 5.1.

Under the conditions prevailing at the end of the electrodialysis, the protein, which will be referred to as protein A, is almost insoluble and is found at the bottom of the cell in the form of yellowish flakes. For the analysis it was washed with alcohol and ether and dried. For most other purposes it was dissolved in distilled water containing a trace of ammonia (p_H 8).

Protein A gives the usual violet biuret reaction and a deep red precipitate with Millon's reagent. Its nitrogen content is 13.8 ± 0.4 per cent (Kjeldahl).

2. *Protein B.*—To the serum which has been freed from the bulk of protein A, crystals of ammonium sulfate are added so as to bring it to half saturation. A small amount of proteins, being a mixture of A and B, separates and is filtered off. The clear filtrate is then saturated with ammonium sulfate at p_H 7.0. Since the dense brown precipitate, which tends to adhere to the walls, separates rather slowly, the mixture is allowed to stand for about 24 hours before it is centrifuged. The sediment, which contrary to protein A, readily dissolves in a neutral or even slightly acid medium, is purified in the same way as described for A. Its transparent brown solution is freed by filtration from impurities precipitated during electrodialysis. The protein, which will be referred to as protein B, is soluble in the absence of electrolytes (p_H ~ 5.3 at the end of electrodialysis).

For preparing large amounts of B, it is convenient to start from a serum obtained by coagulating latex with ammonium sulfate. Three parts of latex are mixed with one part of the saturated salt solution. The slightly opaque serum is filtered through ceramic filters and treated in the same way as described above.

Protein B shows a strong positive biuret reaction, and gives, like A, a red precipitate with Millon's reagent. Its nitrogen content was found to be 15.2 ± 0.5 per cent (Kjeldahl).

C. Properties of Proteins

1. *Electrophoretic Mobility.*—A microcataphoresis cell with platinized platinum electrodes was used for these experiments. It consisted of a flat glass tube with elliptical cross section, to which glass stop-cocks were sealed on at the ends. The electrodes, coiled platinum wires, were fused in, having a distance of 20 cm. from each other. In the center the tube was ground flat and polished, so that the whole depth of the cell (2 mm.) could be observed under a powerful objective lens. A

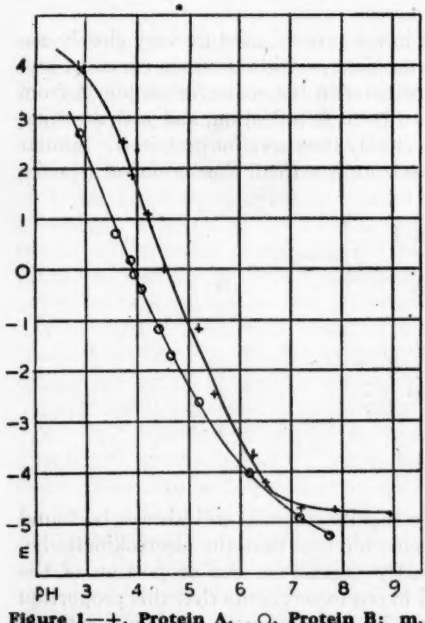


Figure 1—+, Protein A. ○, Protein B; m, Cataphoretic Mobility: μ|sec.|volt|cm.

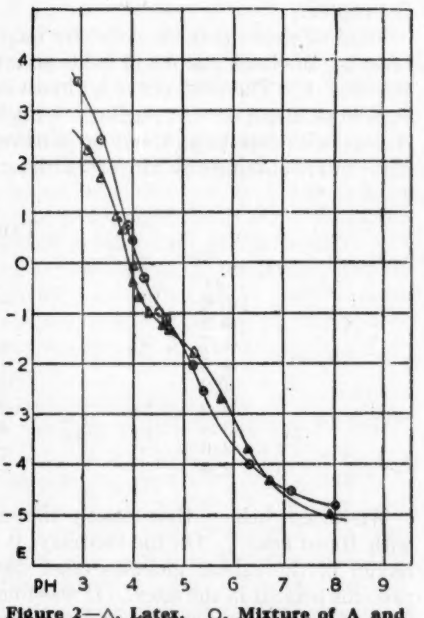


Figure 2—△, Latex. ○, Mixture of A and B; m, Cataphoretic Mobility: μ|sec.|volt|cm.

cross mark assured observations always being made at the same part of the cell. Readings were taken in 1/5th of the depth.[14] The cell was mounted horizontally on the microscope, whose tube, too, was in horizontal position. The current was never passed in one direction for more than 15 seconds, after which time it was reversed and the mobility in the opposite direction measured. No asymmetry due to polarization or liberation of gas was observed.

For determining the electrophoretic mobility, we made use of the well-known phenomenon that protein-coated surfaces of microscopic particles, such as quartz, zinc oxide, and the like, exhibit practically the same electrokinetic behavior as protein itself.[15] Quartz particles having a mean diameter of 2 to 3 μ were used in our experiments. The solutions employed were Sorenson 0.01 *N* phosphate and acetate buffers (B. D. H.), with a protein content of 0.05 to 0.1 per cent. The quartz was first added to the more concentrated protein solution, which was then

diluted to the required strength. The H ion concentration was determined with a glass electrode. The mobility/p_H curves for the proteins are given in Fig. 1. A has an i. p. at p_H 4.55 ± 0.05, B at p_H 3.90 ± 0.05.

It is seen from the graph that the curves for A and B are very similar in shape, but are clearly distinct from each other. A comparison with the mobility curve for latex would, therefore, allow one to decide which of the proteins determines the electrokinetic behavior of the rubber globules.

In Fig. 2 the curves for latex and for quartz, suspended in solutions containing about equal amounts of proteins A and B, are recorded. In the former experiments, one drop of latex was mixed with 2 cc. dialyzed serum and 8 cc. buffer solution. Thus it was possible to avoid the inconvenience of high rubber concentration, without at the same time diluting the solutions to the same extent with regard to the proteins.

Figure 2 shows that the curve for quartz in the protein mixture very closely approaches the latex curve and holds an intermediate position between curves A and B in Fig. 1. The latex curve is almost identical with the curve for protein A from p_H 8 to p_H about 6. At p_H about 5.4 it has a point of inflection, and with a second change in its slope at p_H about 4.4 joins very closely the curve for protein B. Similar curves were obtained by Moyer[16] with latices from American *Euphorbiaceae* (species *Esula*).

TABLE I

	Precipitate	
p_H	A	B
>6.0	−	−
5.2	+	−
4.7	+ +	+
4.5	+ + +	+ +
4.2	+ +	+ +
4.0	+	+ + +
3.8	+	+ + +
3.6	−	+ +
2.9	−	−

We do not believe that exactly the same mobility curves will always be found with *Hevea latex*.[17] On the contrary, it seems obvious that the electrokinetic behavior of the rubber globules must distinctly depend on the proportion of the proteins present in the latex. It was found in our experiments that this proportion is far from being constant, and the sample investigated was one comparatively poor in protein A. It seems, however, safe to assume that the mobility curves for *Hevea latex* will always be intermediate between the curves for A and B.

2. *Precipitation of the Proteins.*—It has become customary to distinguish proteins by their precipitation limits, *i. e.*, the minimum concentrations of neutral salts, such as ammonium sulfate or zinc sulfate, required to start and to complete precipitation.[18] The limiting concentrations of ammonium sulfate necessary for the precipitation of protein A from a 0.01 phosphate buffer were 10.7 to 14.0 g. per 100 cc. (20 to 26-per cent saturation, p_H 6.5 to 6.7). The corresponding figures for B are 32 to 43 g. ammonium sulfate per 100 cc. solution (60 to 80-per cent saturation, p_H 6.6 to 6.8). The upper limit is somewhat uncertain, because complete precipitation of protein B is a lengthy process.

Neither of the proteins is precipitated from 0.01 *N* phosphate buffers (p_H 7.8) by saturation with sodium chloride.

The solubility of the proteins strongly depends on the hydrogen-ion concentration. Both A and B are almost insoluble at their isoelectric points. A, moreover,

once precipitated, does not redissolve in distilled water or neutral sodium chloride solutions, the addition of alkali being necessary to effect peptization ($p_H > 7.8$). Table I shows in a qualitative manner the influence of p_H on the solubility of the proteins.

Ethyl alcohol brings about flocculation of protein A if present in concentrations higher than 60 to 70 per cent (p_H 7.5), but less than 35 per cent of alcohol causes the protein to separate from its solutions at p_H 6.5, if excess electrolyte has been removed by dialysis. PO_4'''-ion seems to have a peptizing effect, since more than 60 per cent alcohol is required to precipitate the protein from 0.05 *N* phosphate buffers of the same hydrogen-ion concentration.

Protein B is not precipitated by alcohol. Moreover, when dried, it is dissolved by 75 per cent alcohol, especially if the latter contains a trace of ammonia.

The influence of some "polar–non-polar" liquids was also studied. It seemed interesting, as the coagulation of lactices by these substances was recently described.[19] Most of the polar–non-polar liquids found to be coagulants for latex in the paper, just mentioned, were also found to make protein A insoluble when its solutions were shaken with one of these organic liquids as a second phase. Amyl alcohol was particularly active. The experimental conditions were chosen so as to resemble the conditions described in the paper just mentioned, *i. e.*, the solutions of A contained small amounts of ammonia and other electrolytes. The protein is strongly adsorbed at the interface, acting as a semisolid emulsifier. When the emulsion ultimately breaks, the protein forms a thick film at the liquid/liquid interface. Non-polar liquids, which do not act as coagulants for latices, also do not show any marked action, when shaken with a solution of A; only a slight denaturation is frequently observed over a long period. Hence, in this case of *Hevea latex* the coagulation by polar–non-polar liquids is probably in part or mainly due to their behavior towards protein A.

Protein B is not affected appreciably by polar–non-polar liquids.

3. *Gold Number.*—The gold number of the latex proteins could not be determined with great accuracy. This is due to the fact that both A and B exert but a feeble protective action on formol gold sols prepared according to Zsigmondy.[20] No concentration within reasonable limits could be found where A prevented the color of the sols changing into blue after the sodium chloride solution had been added. The blue sols, however, did not show any sign of further coagulation if the amount of added protein exceeded 3 to 5 mg. per 10 cc. of sol. The gold number of B was found to be 0.4 to 1, but even at protein concentrations as high as 7.5 mg. per 10 cc. a slight color change was observed. It is interesting to note that gold sols prepared by the phosphorus method, having much smaller particles, are completely protected against coagulation by comparatively small amounts of A or B (0.1 to 0.3 mg. per 10 cc.).

The affinity of the latex proteins to colloidal gold seems to be rather small. This is borne out by the fact that the gold particles are not carried into the interface when the protein-containing sol is shaken with chloroform according to Traube's[21] method. If gelatin is used as protective colloid, the aqueous phase becomes colorless on shaking with chloroform, because the gold is dragged by the gelatin into the liquid/liquid interface.

DISCUSSION

It cannot as yet be ascertained whether the proteins described in this paper are identical with those found in fresh latex. There is, however, some reason to believe that both A and B also occur in freshly tapped latex. Coagulation experiments in particular suggest that these proteins are the determining factors for the stability

of fresh as well as preserved latex.[22] As an example, Fullerton's[22] experiments may be quoted. He finds with diluted fresh latex complete dispersion from p_H 1.0 to 3.5, partial coagulation from p_H 3.5 to 3.8, complete coagulation from p_H 3.8 to 4.8, partial coagulation from p_H 4.8 to 4.9, decreasing flocculation from p_H 4.9 to 5.3, and complete dispersion at p_H >5.4. Very similar results are given for preserved latex, and could be confirmed by our experiments. Complete coagulation extends over the whole range of p_H between the isoelectric points of A and B and becomes less pronounced on the alkaline as well as the acid side of this range.

On the other hand, flocculation experiments with coagulants, other than acids, *i. e.*, alcohol, neutral salts, polar–non-polar liquids, etc., reveal a behavior which seems to be influenced mainly by the properties of protein A alone. Likewise, the electrophoretic mobility of latex particles is identical with that of protein A in alkaline solutions, and only at p_H 5.5, where aggregation commences, is there a break in the mobility curve for latex which now tends to approach the protein B curve. This fact and numerous observations regarding the flocculation and coagulation of latex suggest that normally, *i. e.*, in neutral or alkaline solutions, the single rubber particles in latex are coated with a layer of protein A, which is adsorbed in preference to the more soluble protein B. On the aggregates, however, which form at p_H <5.4, there will be a surface layer consisting of a mixture of A and B, which over a certain range of p_H (4.5 to 3.7) exhibits the behavior of protein B.

Our results make it readily understood why the proteins in *Hevea latex* favor, on the one hand, a concentrated emulsion of rubber particles, provided that the p_H and the electrolyte concentration are suitable; why, on the other hand, owing to the fairly hydrophobic nature of protein A, latex behaves as a somewhat hydrophobic suspension when coagulated by polyvalent cations.

Other authors, when isolating proteins from *Hevea latex*, have usually adopted a different technic. It is, therefore, somewhat difficult to compare the results. Belgrave and Bishop[9] analyzed a protein obtained by precipitation at p_H 4.5. This was probably a mixture of A and B, since both are but sparingly soluble at this p_H (see Table I). The substance, referred to as protein B in Bishop's[9] paper, may be identical with our protein B, whereas his protein C was probably a heat-denatured product.

The protein investigated by Kemp and Twiss[5] appears to have been a mixture of A and B, but consisting mainly of A. Our experiments confirm their result that the behavior of the latex particles is mainly determined by a coating of protein, not of any other substance. But we consider it doubtful whether their results allow a calculation of the fraction of latex-globule surface covered with protein till more is known about the adsorption of the proteins A and B in a mixture of both.

It has not been attempted to classify the latex proteins into any of the well-known groups. Judging, however, from the solubilities alone, protein A will have to be placed in the glutelin or globulin group, whereas the alcohol-soluble protein B might be labelled as prolamin-like gliadin. It remains to be seen whether this view is confirmed, when the proteins are split into their amino acids.

SUMMARY

1. Two proteins were isolated from preserved *Hevea latex*.

2. The proteins were distinguished by their electrokinetic behavior and their solubilities in aqueous solutions and in alcohol. Protein A has an isoelectric point at p_H 4.55; it is insoluble in distilled water and alcohol. Protein B has an iso-

electric point at p_H 3.9; it is soluble in pure water and strong (70 per cent) alcohol.

3. A comparison of the electrophoretic mobility of the latex particles as function of the p_H with the corresponding curves of the proteins confirms the result of previous investigators that a coating of the rubber particles by proteins is decisive for their behavior. In a range of p_H between 5.5 and 8 the curve of the latex particles is practically identical with that of protein A.

REFERENCES

[1] O. de Vries, "Estate Rubber," Batavia, **1920**, 11 *et seq.* Rhodes and collaborators, *J. Rubber Res. Inst. Malaya*, **2**, 125 (1930); **3**, 160 (1932).

[2] W. Clayton, "The Theory of Emulsions," 3rd edition, **1935**, 169–201.

[3] C. O. Weber, *Gummi-Ztg.*, **17**, 652 (1903); *Ber.*, **36**, 3108 (1903).

[4] Belgrave, *Malayan Agr. J.*, **11**, 348 (1923). Freundlich and Hauser, *Kolloid Z.*, **36**, *Zsigmondy Festschrift*, **15** (1925). Sheppard and Eberlin, *Ind. Eng. Chem.*, **17**, 711 (1925). Twiss, *Trans. Inst. Rubber Ind.*, **6**, 419 (1931); and many others.

[5] Kemp and Twiss, *Trans. Faraday Soc.*, **32**, 890 (1936).

[6] Fickendey, *Kolloid-Z.*, **8**, 43 (1911). Frank, *Gummi-Ztg.*, **26**, 1718 (1912). de Vries, "Estate Rubber," p. 153. Scholz, *Kautschuk*, **1928**, 5.

[7] Eaton, Grantham, and Day, *Agr. Bull. Fed. Malayan States No.* **17**, 1 (1918). de Vries and Spoon, *Rubber Age*, **4**, 437 (1923). Bishop, *Malayan Agr. J.*, **15**, 271 (1927). Boggs and Blake, *Ind. Eng. Chem.*, **28**, 1198 (1936).

[8] D. Spence, "Lectures on India Rubber," p. 195 *et seq.*, **1908**. Freundlich and Hauser, *loc. cit.* (4). v. Weimarn, *Bull. Chem. Soc. Japan*, **3**, 162 (1928).

[9] Belgrave, *Malayan Agr. J.*, **11**, 348 (1923). Belgrave and Bishop, *Ibid.*, **11**, 371 (1923). *India-Rubber J.*, **67**, 547 (1924). Belgrave, *Malayan Agr. J.*, **13**, 154, 367 (1925). Bishop, *Ibid.*, **15**, 27 (1927).

[10] F. Frank, *Rubber Ind.*, **1914**, 144; *Gummi-Ztg.*, **29**, 196 (1914). Arisz, *Arch. Rubbercultuur*, **8**, 450 (1924).

[11] The use of ceramic filters is described by E. A. Hauser, German patent No. 412,060 (1923). See also Ditmar, *Caoutchouc & gutta-percha*, **22**, 12,857 (1925); E. A. Hauser, "Latex." Dresden and Leipzig, **1927**, p. 120.

[12] Pauli and Valko, "Elecktrochem. d. Kolloide," Wien, **1929**, p. 369.

[13] Ettisch and Ewig, *Biochem. Z.*, **216**, 440 (1929).

[14] Cf., for instance, H. Freundlich, "Kapillarchemie," Leipzig, **1930**, vol. 1, p. 344.

[15] Freundlich and Abramson, *Z. physik. Chem.*, **133**, 51 (1928). Abramson, *J. Am. Chem. Soc.*, **50**, 390 (1928). Lindau and Rhodius, *Z. physik. Chem. A.*, **172**, 321 (1935).

[16] Moyer, *Am. J. Botany*, **21**, 293 (1934).

[17] Cf., for instance, Kemp and Twiss, *loc. cit.* (5).

[18] Cf. "Allen's Commercial Organic Analysis," London, **1913**, vol. 8, p. 65.

[19] Daniel, Freundlich, and Söllner, *Trans. Faraday Soc.*, **33**, 890 (1937).

[20] R. Zsigmondy, "Lehrbuch d. Kolloidchemie," 1st ed., **1912**, 94.

[21] Traube and Rackwitz, *Kolloid-Z.*, **37**, 131 (1925).

[22] Cf., for instance, de Vries and Beumée-Nieuwland, *Arch. Rubbercultuur*, **10**, 503 (1926); **11**, 518 (1927); **12**, 683 (1928). van Harpen, *Ibid.*, **11**, 487 (1927); **12**, 432 (1928); **13**, 61 (1929). Fullerton: *J. Rubber Res. Inst. Malaya*, **2**, 156 (1930)

[Translated for Rubber Chemistry and Technology from the Kolloid Zeitschrift, Vol. 84, No. 1, pages 63–74, July, 1938.]

The Creaming of Hevea Latex by Colloids

C. F. Vester

Research Division of the Rubber Institute, Delft, Holland

INTRODUCTION

Hevea latex is generally considered to be a suspension of rubber particles of various dimensions up to about 3 μ.[1] The rubber hydrocarbon contains no "ionogenic groups," and it is believed that part of the serum components imparts a negative charge to the rubber particles.[2]

Almost all latex imported into Europe is preserved by means of 0.5 to 0.7 per cent of ammonia. This ammonia plays a three-fold part: (1) it prevents premature souring of the latex; (2) it increases somewhat the charge[3] on the particles; and (3) it attacks all types of serum components so that within a short time the "preserved" latex is hardly comparable with natural latex.

As with all suspensions in which the dispersed phase is lighter than the dispersing medium, rubber latex exhibits the phenomena of creaming. The density of the rubber particles is approximately 0.914, that of the medium, 1.020.

By means of creaming, it is possible to obtain a latex (1) which has a higher rubber content, whereby transportation space and cost are saved, and (2) which contains no components having a tendency to deposit a sediment.

The natural creaming of latex, which is of no importance technically, was observed by Faraday[4] as early as 1825.

Only in ideal cases, *i. e.*, when the particles are spherical and the sols are not too concentrated, is the Stokes law[5] valid:

$$V\uparrow = \frac{2g(D_m - D_k)}{\eta} r^2$$

where $V\uparrow$ is the velocity of rise of the spheres, g is the acceleration due to gravity (981.2), $(D_m - D_k)$ is the difference in densities of the medium and spheres, r is the radius of the particles, and η is the viscosity of the medium.

As is evident from this formula, the size of the particles is of predominant importance, for the velocity of rise increases in direct proportion to the square of the radius. In this formula of Stokes, four of the factors, *viz.*, D_m, D_k, η, and r, depend on the temperature.[6]

ACCELERATED CREAMING BY MEANS OF CREAMING AGENTS

Génin credits Fickendey[7] as the first to employ biocolloids for accelerating creaming. However, Fickendey used a 10-per cent solution of protein to stabilize *Castilloa* latex, and was not concerned with creaming.

In 1923 Traube[8] obtained a patent for a process for the production of a latex cream by means of biocolloids. Since then, many variations of this method of concentration have been proposed, yet even now the phenomena involved in creaming are not fully explained.

All creaming agents of plant origin form extremely viscous liquids when in 1 to 2-per cent solutions in water. They swell greatly in water and are capable of com-

bining with large proportions of water. They are of a highly complex nature, and many of their decomposition products are the same, irrespective of the creaming agent. Experience has shown that the viscosity of these substances increases with increase in size of their complex units.

In the following brief review of the most important of these agents, the latter are classified according to their ionogenic groups.

1. Sulfate Colloids

(*a*) *Carrageen.*—Carrageen is a component of various seaweeds, *e. g.*, *Chondrus crispus*, and is obtained by extracting these plants with cold[9] or warm[10] water. According to Teunissen,[11] very pure carrageen contains 10.9 per cent of sulfur.

(*b*) *Agar-agar.*—Agar-agar is a product, the chemical composition of which is related to that of carrageen, and in it, too, calcium is the natural counter ion. The sulfur content is lower than that of carrageen. However, still other ionogenic groups are present, and it is generally agreed that the ratio of the number of sulfate groups to carboxyl groups is 2:3.

2. Carboxyl Colloids

(*a*) *Pectin.*—According to Ehrlich[12] pectin occurs in fruit as the "calcium-magnesium salt of pectinic acid," *i. e.*, as "neutral pectin."[13] By acid hydrolysis the latter is decomposed into 4 molecules of galacturonic acid, 2 molecules of methyl alcohol, 2 molecules of acetic acid, 1 molecule of arabinose, and 1 molecule of galactose. The 4 molecules of galacturonic acid are combined in a cyclic complex in pectin. This tetragalacturonic acid is therefore a "polysaccharidic acid" or a "carboxylated pentosan," $C_{20}H_{28}O_{16}(CO_2H)_4$.

(*b*) *Alginates.*—Salts of alginic acid (polymannuronic acid $-$ $A = C_{21}H_{27}O_{20}$), which is probably a dibasic acid, are obtained by extraction of seaweeds, especially of the *Laminaria* type, with soda. Only the alkali salts of this acid are soluble in water; with other metal ions insoluble compounds (alginoids) are formed. The Société Otam manufactures a preparation by the name of "pure ammonium alginate," which is not pure ammonium alginate at all. Purification of such a commercial product would be too costly.

(*c*) *Tragacanth* (*gum tragacanth*).—Good tragacanth from Smyrna is an excretory product of certain kinds of *Astragalusa*. Inferior tragacanth frequently contains considerable starch. Some of the decomposition products of tragacanth[14] are the same as those of pectin, *e. g.*, *d*-galacturonic acid.

(*d*) *Lichenins.*—Lichenins are "reverse cellulose" of the cell walls of *Cetraria islandica* and *Usena barbata*. The lichenin of the cell walls forms a colloidal solution in boiling water. It is less soluble in cold water.

(*e*) *Hemicelluloses.*—Like lichenin, hemicelluloses are reserve substances in the cell walls. Among them are mannan and galactan. They dissolve in water very slowly. (*i*) *Galactans.*—To this group belongs Karaya gum or Indian gum. According to Turner[15] this is a product of the *Sterculia urens*. It is frequently used as a substitute for tragacanth, because Karaya meal is cheaper. It dissolves more rapidly than does tragacanth, and gives an acid reaction in water. (*ii*) *Mannans.*—The seeds of *Ceratonia siliqua L.* (locust bean and carob bean) from countries on the Mediterranean Sea, particularly Cyprus, are very rich in mannan. The seeds are extracted with water at 70–80° C.; the mucilaginous product is obtainable under the name Tragasol,[16] and in powder form as Tragon. When hydrolyzed in acid medium, pure mannans form only *d*-mannose. (*iii*) *Glucomannans.*—*Amorphophallus konjaku* contains a mannan[17] which on hydrolysis yields

not only mannose but also glucose, and therefore appears to be a glucomannan. The mannan content of Japanese tubers is said to be 43 to 68 per cent.

Tubers of *Amorphophallus variabilis* are collected in Java, are cut into slices, and are dried. Kraay[18] was the first to prove the creaming power of *Amorphophallus* powder. The latter swells greatly in water and forms a very viscous liquid, which putrefies rather rapidly, with resulting decrease in viscosity and deposition of a solid substance. The powder prepared from Japanese tubers swells to a greater extent than does that from Javanese tubers.

SYNTHETIC CREAMING AGENTS

Besides the colloids of plant origin which have just been mentioned, synthetic creaming agents have recently been discovered. The best known of these is sodium polyacrylate,[19] which according to Staudinger has the constitution: $[-CH_2CHCO_2Na]_x$. For a degree of polymerization of $x = 200$, the "molecular weight" would be 18,800.

In the most recent literature, more data[20] on other colloids which have creaming power are to be found, but those already mentioned above are still the most important. Among semi-synthetic substances might be included methylated carbohydrates, *e. g.*, tylose,[21] which is a mixture of mono- and dimethylcellulose (about 1.5 methyl-). This substance should be dispersed in hot water, and then swells only after cooling, forming an extremely thick solution.

EXPERIMENTS ON CREAMING

The object of the investigation to be described was to obtain more information on the part played by strongly hydrophilic colloids in the creaming process. Certain other purposes of the investigation which are mentioned below were primarily to explain various phenomena involved in creaming. In this work there has been no intention of giving preference to any particular creaming agent.

Latex of 40-per cent concentration and preserved with ammonia was used in all the creaming experiments. To obtain strictly comparable results, 80 cc. of 40 per cent latex and 20 cc. of the solution of creaming agent were mixed together in every case. These two liquids were then mixed very thoroughly.[22] The mixture was poured into a calibrated cylindrical 100-cc. separatory funnel.

When this method is used, creaming is estimated by the appearance of a visible plane of separation between the cream and the under layer. The speed of creaming is therefore estimated by the rate at which this plane of separation rises. Separation of the layers is not always satisfactory however, and especially at the beginning, during the so-called induction period, the plane of separation is invisible in spite of the fact that the rubber content in the upper part of the liquid has already commenced to increase.

INFLUENCE OF THE QUANTITY OF CREAMING AGENT

The formula of Stokes shows that an increase in viscosity of the medium hinders the rise of the particles, and it is therefore obvious that an increase in concentration of the creaming agent does not necessarily result in any increase in the speed of creaming. On the contrary this rate is frequently retarded, as may be seen by the graphs in Fig. 1 and Table I.

The horizontal broken lines in the figures show the volume Z (in most cases 20 cc.) of a solution of the creaming agent which was added to the latex. Hence concentration may be said to have taken place only when the curve of creaming has reached a point above this horizontal line.

The curves in Fig. 1 show that mixtures A and B, which contained 0.2 per cent of tragacanth, creamed more rapidly than did mixtures C and D, which contained 0.4 per cent of tragacanth. It should also be noted that curves A and B coincide throughout, whereas curves C and D remain apart. Then again the progress of creaming of mixtures C and D was much more irregular. This difference is attributable to the fact that during creaming separation ("breaking") of the system

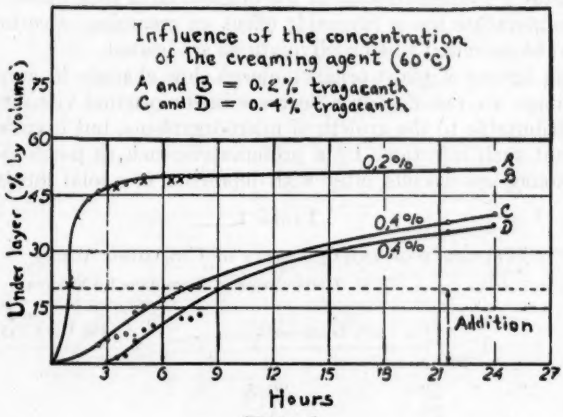


Figure 1

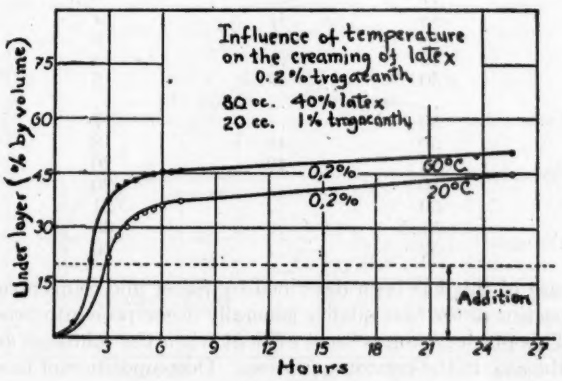


Figure 2

occurs, and in mixtures A and B, which contained only relatively small amounts of creaming agent, the coherent masses were smaller than they were in mixtures C and D.

In the latter cases creaming progressed in a pulsating manner, and this phenomenon was promoted by the higher viscosity. This phenomenon is also evident in Fig. 3, which shows the result of creaming by means of Citrus pektin-160.

In general, the lower layer is clearer when a relatively large amount of creaming agent is used.

INFLUENCE OF TEMPERATURE

With increase in temperature the viscosity decreases, and as a result an acceleration of creaming is to be expected. This influence of temperature varies with the choice of creaming agent.

Figure 2 shows the results of a few experiments with tragacanth, and Fig. 3 shows the influence of temperature on the mixture containing Pektin-160. It is evident from Fig. 3 that after 24 hours of creaming by 0.4 per cent of Pektin-160 at 20° C., practically no further concentration of the original latex took place. Although an increase in temperature has a favorable effect on creaming, a certain amount of caution should be exercised when such mixtures are heated.

All creaming agents of plant origin undergo slow changes in aqueous solution, and these changes are manifest in a decrease in the original viscosity. This may be in part attributable to the growth of microörganisms, but even when it is possible to prevent such infections by a preservative such as *p*-chloro-*m*-cresol, the liquid still becomes less viscous, often with deposition of a solid substance.

TABLE I

INFLUENCE OF THE QUANTITY OF CREAMING AGENT

Time in Hours	Under Layer in Percentage by Volume			
	0.2 Per Cent Tragacanth		0.4 Per Cent Tragacanth	
	A	B	C	D
1	23	20.5	..	..
1.5	39	..	..	..
2	44	..	..	..
2.5	46	..	5	..
3	47	..	6.5	..
3.5	48	47	7	1
4	48	..	8	2
4.5	49	..	14	6
5	50	49	15	9
5.5	..	..	..	10
6	50	..	17	..
6.5	50	49	18	..
7	50	49	20	12
7.5	50	..	20	12
8	50	..	21	13
21.5	51.5	..	38	35
24	52	..	40	37

A typical case of this has been described by Sauer and Sanzenbacher.[23] They showed that pectins of the best quality generally decompose into products of lower viscosities. This phenomenon is most evident when the solutions are warmed, as is frequently the case in the creaming process. Decomposition of this kind is much more rapid in alkali and ammoniacal media.

In this connection it should be pointed out that the lower layer changed color according to whether creaming was carried out with or without warming the mixture. Without warming or with gentle warming, *i. e.*, below 30° C., the layer which separated below the cream was much clearer than it was when the latex was heated to higher temperatures, and frequently was almost transparent and of an amber color. Evidently, therefore, at relatively high temperatures (above 60° C.) or by excessively long heating, decomposition sets in, and the decomposition products are less active.

In this same connection, the following experiments, which were carried out with substances of various particle sizes, may be described:

(*a*) The results of creaming by pectin of the best quality (Citrus pektin-160) at 60° C. are shown in Fig. 3. In this case 0.2–0.4 per cent and 1 per cent of pectin were used for creaming, and it is evident that creaming was not accelerated by increasing the concentration of this creaming agent.

(*b*) A comparison of the curves in Figs. 3 and 4 shows at once that in the latter case the results were less satisfactory, for Pektin-80 required about twice as much creaming agent to obtain the same depth of layer. Furthermore with 0.4 per cent of the lower grade pectin, the plane of separation was scarcely visible.

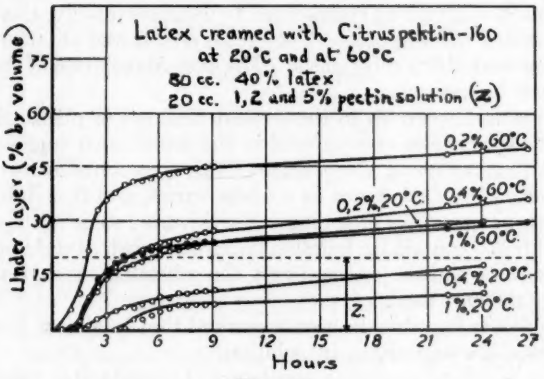


Figure 3

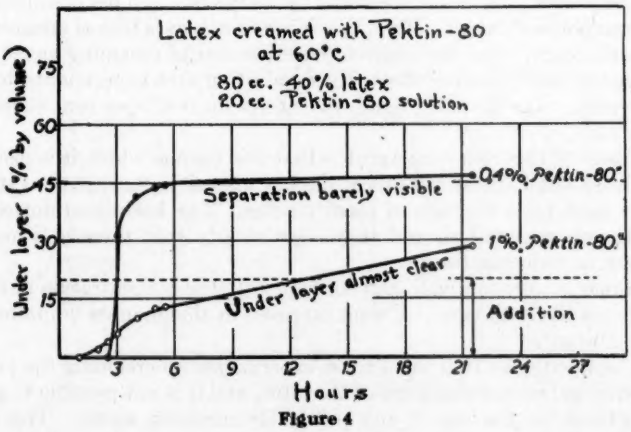


Figure 4

(*c*) The results with substances of small particle size were very unsatisfactory, *e. g.*, with tetragalacturonic acid, which was used in the form of its ammonium salt. These results are shown in Fig. 5. In this experiment the stratification was almost invisible during the first 15 hours, for the under layer and the cream showed no differences in color.

These experiments confirm the assumption already made, *viz.*, that the more complex the structure of a creaming agent, and the greater the number of its unitary particles in colloidal solution, the greater is the creaming power of the substance.

The viscosity of mucin-like substances of this kind is a rough measure of the size of its particles. In general then, the higher the viscosity of a solution of creaming agent, the greater the activity of the particular substance as a creaming agent.

STRATIFICATION

The liquid does not always separate into two layers; frequently a third thin layer between the cream and the lower layer of serum is visible.

This phenomenon is shown in Fig. 6. In this case creaming was carried out by means of a suspension of powdered *Amorphophallus* tubers.[24] The shaded area on the diagram represents the extent of existence of this intermediate layer. At the time when the speed of creaming commenced to decrease rapidly, this intermediate layer also commenced to disappear. The cream which was obtained in this way contained 59.1 per cent of dry substances. The aqueous solution of the powder had a strong tendency to ferment.

All creaming agents known up to the present time are of plant origin, and difficulties have frequently been encountered in the use of such substances. In addition to the active component, a substance of this type contains inert substances, so that the activity of the substance as a whole varies, and it is difficult to know what proportion is necessary for creaming. Furthermore some of these products in their commercial forms contain undesirable impurities, such as residues of cell walls and similar extraneous matter. Accordingly the substances should almost always be purified before they are used.

In the third place, it has already been remarked that in almost every case they undergo hydrolytic decomposition in solution.

In view of this, synthetic creaming agents are of considerable value, and therefore experiments were carried out with these substances.

Figure 7 shows the progress of creaming by means of 0.125 per cent and 0.25 per cent of sodium polyacrylate.[25] Here, too, it is evident, as is true of creaming agents of biosynthetic origin, that the highest concentration of creaming agent not only does not give the best creaming effect, but in addition such experiments do not give consistent results. On the other hand, the curves for 0.125-per cent concentration almost coincide.

An advantage of this creaming agent is that the volume which it is necessary to add is relatively small, for as a result of the low viscosity, concentrated stock solutions can be used, as in the case of plant mucins. The horizontal dotted lines in Fig. 7 are therefore very low, and they show clearly that there is a much more rapid increase in concentration.

The substance is easy to weigh, and consequently the concentration of the active proponent is not likely to vary. Cream prepared in this manner contained 65 per cent of dry substances.

It should be mentioned that in all these experiments on creaming the progress of creaming depended on the character of the latex, and it is not possible to give complete instructions for the use of any particular creaming agent. The creaming agents mentioned above give in every case, at the concentrations designated and at 60° C., creams containing 56 to 60 per cent of dry substances. Tylose S-400, which is a mixture of methylated products of cellulose, gives poorer results as a creaming agent, especially when the system is warmed.

EXPLANATION OF THE MECHANISM OF CREAMING

1. Agglomeration

It is generally expected of a true cream that it can be converted back into normal latex by dilution with ammoniacal water. Its concentration is also reversible. It

is known from studies of the chemistry of milk that creaming involves the formation of very loose agglomerates, which are frequently difficult to observe.[26]

Hence it is probable that in latex as well this agglomeration is promoted in some way by the creaming agent. Normal latex cream is however "optically filled" to such a degree that it is unsuitable for direct microscopical examination. If a little cream is added to water, no visible aggregates are formed, but only free rubber particles in lively Brownian motion. In spite of this, however, the liquid which separates as an under layer when creaming is complete is in osmotic equilibrium

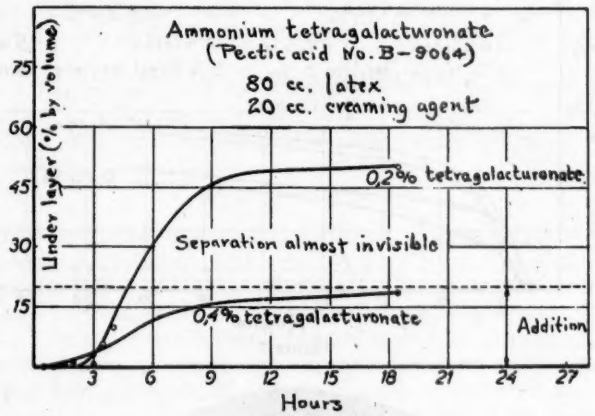


Figure 5

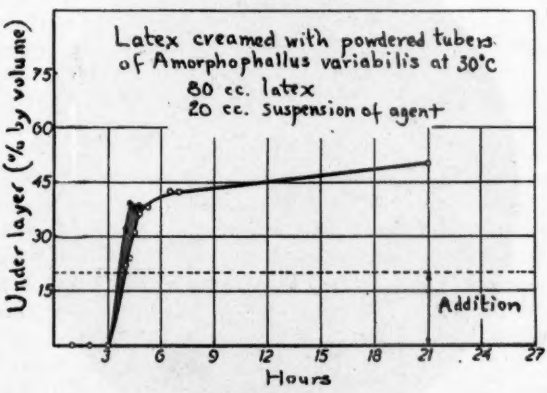


Figure 6

with the cream. This "equilibrium liquid" is better adapted as a diluent for preparing samples for microscopic examination. By this means it is possible to render the agglomerates visible, as shown in Fig. 8 (magnification of 160).

In this way it can be shown that creaming agents actually do aid agglomeration, but that the rubber particles retain their individuality, and that after addition of water the agglomerates rapidly break up into free discrete particles, and therefore that when the cream is diluted a "regenerated latex" is obtained.

In view of all this, it is understandable why artificial creaming proceeds more

rapidly than does natural creaming; for the dimensions of the aggregates are much greater than those of the individual particles, and with increase in size the speed of rise through the liquid increases greatly.

Soon after this experimental investigation was completed, Baker[27] published the results of experiments on creaming and, by means of exceptionally fine photo-

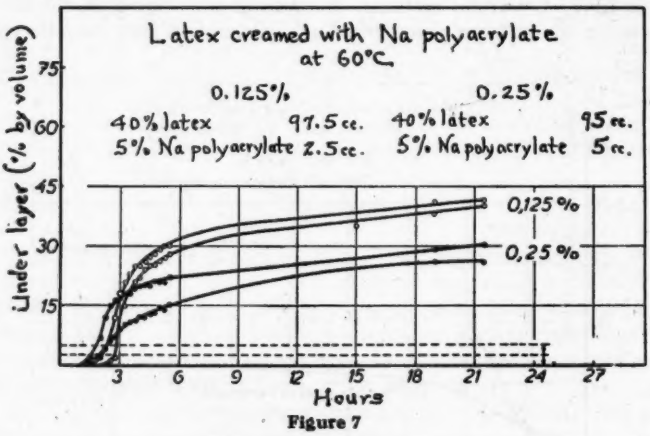


Figure 7

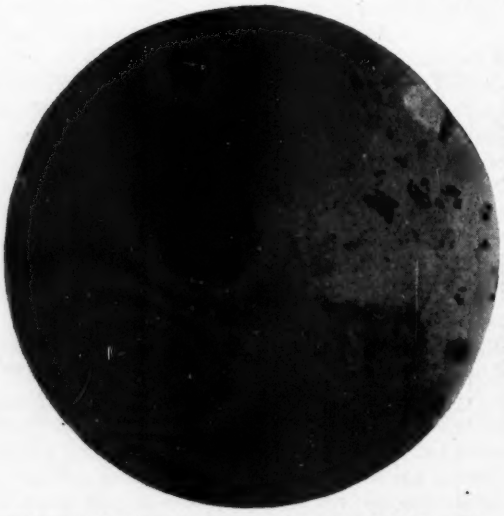


Figure 8—Agglomerates of Rubber Particles in Latex Cream Diluted with Serum (Magnification 160)

graphs, showed the agglomeration of latex particles. His technic for rendering aggregation visible differed somewhat from that already described. For instance, Baker used a very dilute latex, and mixed it with a quantity of creaming agent sufficient to cream normal latex. The formation of aggregates and their separation in water has thus been established beyond a doubt.

The question then arises, to what extent the system can be destroyed by vigorous agitation, after creaming is complete, and what is the character of the creaming which recurs.

A mixture of 80 cc. of latex (40-per cent concentration) and 20 cc. of tragacanth solution (1 per cent) was allowed to cream. This process is shown in Fig. 9 (Curve 1). After creaming was complete, the funnel was allowed to stand for awhile longer, was then agitated vigorously, and again the contents were allowed to cream. Curve 2 in Fig. 9 shows that this second creaming commenced sooner, and in the first part of its progress proceeded about three times as rapidly. When this second creaming was interrupted after about 4 hours by renewed agitation of the liquid, the third creaming which followed proceeded at almost exactly the same rate as did the second creaming.

From this it may be concluded that the agglomerates are destroyed to a large extent by agitation, and that the "induction period" is shortened. Evidently during this first period a second process besides the purely mechanical part of the creaming process takes place.

DROP FORMATION

Microscopic examination of various creams frequently gives one the impression that the aggregation of rubber particles is not merely simple agglutination, for at times the agglomerates show a sort of "fluidity." The rubber particles are to a certain extent able to move past one another as if there were a viscous fluid among these particles. Hence it was desirable to use a latex with a minimum rubber content. Great difficulties are encountered in centrifuging an undiluted 40 per cent latex preserved with ammonia in a small Sharples supercentrifuge, because the cream accumulates in the cylinder and proper functioning of the apparatus is prevented by clogging of the small passages. If the problem is to work up rather large quantities of undiluted latex, a preliminary centrifuging in an apparatus better suited to the purpose would be of advantage. The following technic is, however, preferable.

A can of latex which had stood quietly for about two years was cautiously opened. It was found that a thick white cream had formed. The under layer was carefully removed by means of a syphon, and was allowed to stand for a week. In this way, a deposit of black colloidal metal sulfides and a thin layer of cream on the surface of the liquid were formed. The desired layer was again removed by syphoning, the process was repeated once more, and the latex (containing 12.5 per cent of dry substances) was centrifuged. Because of the low rubber content, no difficulties were encountered in the use of a small Sharples supercentrifuge. The latex obtained in this way, which had a low rubber content, was still white and contained 10.2 per cent of dry substances. Because of the small quantity of this latex available, the true rubber content could not be determined.

The particles in this latex were very small, and the largest ones were scarcely visible under an ordinary microscope.

When this latex of low rubber content was carefully mixed with a solution of a creaming agent, an emulsion formed after a short time, as shown in Fig. 10. This microscopic picture shows a large number of drops, of various dimensions, of a rather viscous liquid in a slightly viscous medium. In a freshly prepared sample for the microscope, the drops were distributed fairly regularly over the area; later they commenced to cream, and the largest drops rose to the cover glass. Here and there two drops slowly combined to form a larger individual drop. By pressing the cover glass lightly or by sliding it, streaks (Schlieren) formed, and these slowly contracted again to drops. Under these conditions all kinds of irregular forms

appeared, as shown in Fig. 11. The surface tension of these drops was evidently slight.

When the solution of creaming agent was mixed with distilled water instead of with latex, this phenomenon did not appear, and therefore the drops were probably formed by combination of the active components in the creaming agent with one or more of the serum components in the latex.

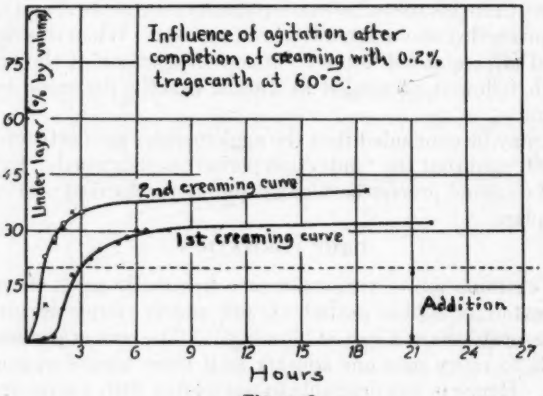


Figure 9

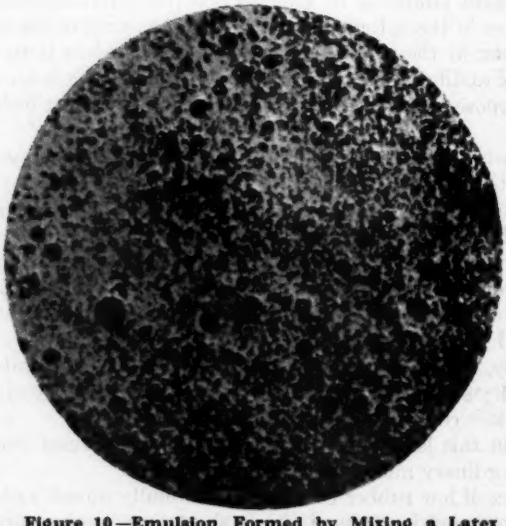


Figure 10—Emulsion Formed by Mixing a Latex Having a Low Rubber Content with a Solution of Tragacanth (Magnification 110)

The droplets contained very small particles which were observed only with difficulty, and in the larger drops, in which they evidently were present in the greatest numbers, they could move about. When attempts were made to stain these droplets by suitable agents, the whole system was altered to such an extent that the droplets soon subdivided into extremely small free particles.

This microscopic examination serves to throw further light on the nature of the creaming process. The latter is perhaps explainable on the assumption that the rubber particles, originally in Brownian motion, become enveloped by a small amount of the discontinuous phase and combine into larger complex units.

If the latex has a very low rubber content and the particles are very small, as in the case described above, visible droplets are formed. On the other hand when the rubber content is high, only the agglomerates already described are visible.

The enveloping mass does not depend solely on the small quantity of creaming agent, for the serum components of the latex, and also water, form part of the enveloping shells.

REPEATED CREAMING

Centrifuging latex gives an opportunity to obtain a highly purified cream. The cream thus obtained can be diluted with water (with or without ammonia) to the original volume, and a new cream can be obtained from this "regenerated latex" by centrifuging again. This method of purification can be repeated several times without any major difficulties. However, when only creaming agents are employed, complications arise. There is no question about the possibility of obtaining a purified cream in this way, but in practice serious difficulties are encountered. For example, serum components are removed by water at each step of the purification. Creaming becomes progressively slower, and finally can hardly be called accelerated creaming. With progressive purification the tendency of the latex to cream decreases progressively.[28]

If the idea is not to purify the latex but primarily to concentrate it, a process is available[29] whereby the serum components are utilized to better advantage in the creaming process. Nevertheless, exhaustive purification of the cream by means of creaming agents should be possible if at the same time a substance were added which has the power of replacing the serum components lost in the reversible formation of complex products. With the aid of such a substance, it should also be possible to accelerate creaming still more, because the formation of a coherent mass enveloping the particles would be facilitated.

ANALOGY WITH THE CREAMING MILK

Various phenomena observed in the creaming of latex show a certain analogy with those observed in the creaming of milk. As has been shown by Rahn,[30] some colloids accelerate the creaming of milk in spite of increasing the viscosity of the mixture. When, however, non-colloidal substances, *e. g.*, sugar, which increase viscosity, were added, creaming was retarded. The acceleration of creaming is therefore a specific property of the creaming agent. Rahn found that the fat globules in fresh milk are capable of combining into units of greater complexity. Creaming agents aid this agglomeration by forming a gelatinous envelope around the particles. Warming often has an unfavorable effect, for then the particles are not always held sufficiently well within the enveloping substance, and rise through the milk as separate particles. Furthermore, van Dam, Sirks, and van der Burg[31] found that tragacanth, gelatin, agar-agar, starch, Iceland moss, etc., accelerate the creaming of milk, and found that during creaming under these conditions there was an aggregation of the fat globules.

Troy and Sharp[32] have pointed out that it is frequently very difficult to see these aggregates because of their loose cohesion. Then again, the number of particles in these aggregates varies, sometimes to a considerable extent. Troy and Sharp agree with Rahn, van Dam, and Sirks that the aggregates contain rather large quantities of milk plasma.

The remarkable phenomenon which is observed when fresh milk is mixed with apple pectin (Pomosin-X) was studied by Kieferle and Sonnleiter.[33] After standing for a few hours, two layers are formed; one of these layers is a kind of equilibrium liquid, the other is an emulsion which contains almost all of the protein of the milk (chiefly casein). These investigators call particular attention to the fact that the formation of this pectin-protein emulsion is a reversible process, in contrast to coagulation by acids or by rennet. The precipitate of protein dissolves rapidly and completely again in water, and consequently no denaturing takes place. A precipitate of casein can also be obtained in this way from skim milk. This phenomenon is not explained. Ziegelmayer[34] reports that, according to a personal communication from Ripa, there is no known method of separation of mixtures of casein and pectin.

EXPERIMENTS WITH AN EMULSION OF PARAFFIN

As a means of comparison with latex, an emulsion was prepared which, after cooling, contained approximately 40 per cent of solid paraffin and was stabilized by a 2-per cent ammoniacal solution of technical casein. The fused paraffin was emulsified in a Hurrell emulsifier in the usual manner.

In the course of time this emulsion creamed slightly, with formation of an under layer which was turbid and resembled a casein sol.[35] When, however, a creaming agent was used, the under layer was clear. This indicates an essential difference between these two creaming phenomena. A reciprocal action between the casein and the creaming agent takes place in some way. Also after mixing casein with tragacanth solution, an emulsion can be observed microscopically, and after about 24 hours it is possible to observe the separation macroscopically.

A concentrated paraffin cream shows, in its equilibrium liquid, a form similar to that of the cream of latex, although of a coarser structure and, as in the case of latex cream, free particles are present after dilution with ammoniacal water.

The experiments with emulsions of paraffin which are described above suggested an investigation of the creaming of latex to which casein has been added. A comparison of the creaming of the following two mixtures A and B:

A		B	
Latex (40 per cent)	80 cc.	Latex (40% per cent)	80 cc.
Tragacanth (2 per cent)	10 cc.	Tragacanth (2 per cent)	10 cc.
Water	10 cc.	NH_4 caseinate (2 per cent)	10 cc.

the results of which are recorded in Fig. 12, show that mixture B, which contains protein, creamed more rapidly. The so-called induction period was greatly shortened, whereas after about 20 hours the creaming effects had become practically the same. Evidently then protein plays a part in the creaming process.

That the serum components of latex have an adverse effect on the tendency of the latex to cream has been shown, for example, by Kraay[36] with latices of various origins. On the other hand, addition of various substances such as proteins may increase the tendency of a latex to cream.

EXPLANATION OF THE FORMATION OF AN EMULSION

Clayton[37] has pointed out that the nature of the creaming of milk, particularly the functioning of creaming agents and the part played by the plasma, has not yet been explained satisfactorily. He emphasizes the fact that the addition of colostrum, which has a high protein content, accelerates the creaming of the fat in milk. Furthermore, according to the opinion of Clayton, attempts should be made

to correlate this with the phenomena described by Tiebackx[38] and with the views of de Jong.[39]

A full explanation of the creaming process in this manner is not, however, so easy in the case of latex, for exact data on the nature of the components which react reciprocally with the creaming agent are lacking.

As an explanation of creaming by means of colloids, simple coacervation would

Figure 11—The Same Drops Shown in Figure 10 but after Pressing the Cover Glass (Magnification 110)

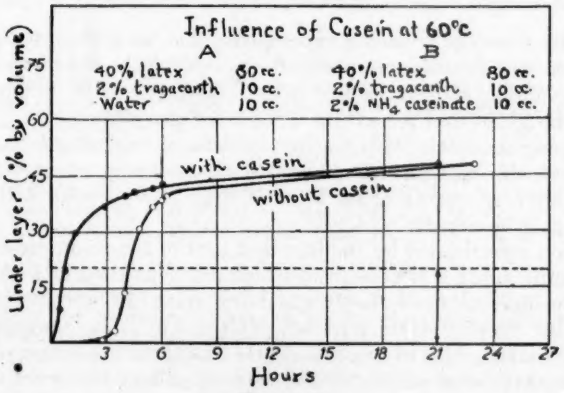


Figure 12

be the first obvious answer. No evidence has been found that the components have opposite charges. The whole phenomenon takes place in an ammoniacal medium, and therefore all components probably are charged negatively. In this case coacervation might be regarded as a reciprocal desolvation through addition of a second colloid. Phenomena of this kind appear, for example, when protein sols and sols of polymeric carbohydrates are mixed. The first examples were described by Beyer-

inck,[40] and similar experiments were carried out by Ostwald and Hertel.[41] The concentrations of the colloids were rather high in the experiments of the latter investigators, but as a matter of fact a 0.25-per cent agar-agar solution and a 1-per cent gelatin solution are said to exhibit this same phenomenon.

If only the alkaline range is considered, *i. e.*, the range within which the particles are all negatively charged, there arises the question already put by Ostwald and Hertel, *viz.*, what is the cause of this kind of separation? A chemical reaction should not even be considered, for well defined compounds of proteins and carbohydrates have not yet been prepared in this manner. The only alternative explanation of the process of separation is then a reciprocal desolvation of similarly charged lyophilic sols.

Since the swelling of many colloids depends on the p_H value, the latter will, in spite of the sign of the electric charges of the components being the same, still have an influence on the phenomenon. According to Duclaux,[42] mucin-like substances such as carrageen and tragacanth are both capable of forming coacervates with protein substances. However, Duclaux offers no explanation of the way in which these are formed, and says only that "they are in all cases complex systems which defy attempts to explain them on a theoretical basis. An explanation would seem to be particularly difficult in the case of these mixtures, for the components themselves are not sufficiently well understood for one to be able to draw any conclusions as to their mutual reactions. Then again, no study of their chemical nature is to be found in the literature of the subject, an absence which is much to be regretted."

In view of these facts, the reciprocal reaction between the serum components of latex and those of creaming agents in the creaming of latex is to be regarded as reciprocal desolvation.

RÉSUMÉ

The origin and the nature of the most important creaming agents are reviewed in a brief way.

It is shown by means of creaming experiments that for a given temperature and quantity of creaming agent, certain conditions relative to the viscosity and stability of the mucin-like substances used in the mixture should be fulfilled. Incidentally it should be added that the nature of the latex also plays a part.

It is shown experimentally that the acceleration of creaming by means of colloids depends on the agglomeration of rubber particles to larger complex units. This agglomeration is reversible, for after dilution of the cream with water, free particles are again observed.

Agglomeration is facilitated by the fact that part of the serum substances forms with the creaming agent a viscous mass which envelops the particles. This phenomenon can be observed more closely with latex which has been specially prepared with a low rubber content for the purpose. In this way it was shown that droplets are formed and that they are to a certain degree analogous to a coacervate. Similar phenomena have been observed in the chemistry of milk and they may be explained in the same way.

ACKNOWLEDGMENT

The author wishes to express his appreciation to the Rubber Institute at Delft for permission to publish these results. He also wishes to thank A. van Rossem, Director of the Research Division, most sincerely for the advice which was offered in the course of the investigation, and also to thank Mrs. A. C. de Leeuw-Sloep for making the photographs.

REFERENCES

[1] A. van Rossem in J. Alexander's "Colloid Chemistry," IV, 235, New York, **1932**; H. Freundlich, "The Chemistry of Rubber," London, **1935**; H. P. Stevens and W. H. Stevens, "Rubber Latex," 4th Ed., London, **1936**.

[2] G. Génin, "Chimie et Technologie du Latex," Paris, **1934**; Kemp and Twiss, *Trans. Faraday Soc.*, **32**, 890 (1936).

[3] Wo. Pauli and E. Valkó, "Kolloidchemie der Eiweisskörper," Dresden, **1933**, 69.

[4] Faraday, *Quart. J. Sci.*, **21**, 19 (1825).

[5] Cf. Duclaux, "Suspensions et Emulsions," Paris, **1934**, 4.

[6] Sharp, *Dairy Sci.*, **11**, 259 (1928).

[7] Fickendey, *Kolloid-Z.*, **8**, 43 (1911); G. Génin, "Chimie et Technologie du Latex," Paris, **1934**, 38.

[8] Traube, German patents 414,210, 414,930 (1930); British patent 226,440 (1924).

[9] Haas, *Biochem. J.*, **15**, 469 (1921); *Kolloid-Z.*, **30**, 206 (1922).

[10] Buttler, *Biochem. J.*, **28**, 759 (1934); Haas, Russell, and Wells, *Biochem. J.*, **16**, 578 (1922); **17**, 696 (1923); **23**, 426 (1929).

[11] P. H. Teunissen, *Thesis*, Leyden, **1936**, 35.

[12] Ehrlich, *Chem.-Ztg.*, **41**, 197 (1917).

[13] A. C. Sloep, *Thesis*, Delft, **1938**, 47.

[14] H. Pringsheim and D. Kruger, "Handbuch der Pflanzenanalyse," Vienna, **1932**, III/1/II, 60; Ehrlich, *Chem.-Ztg.*, **41**, 197 (1917); Weinmann, *Ber.*, **62**, 1637 (1929); *Biochem. Z.*, **236**, 87 (1931); Norman, *Biochem. J.*, **25**, 200 (1931).

[15] Turner and Fuller, *Ind. Eng. Chem.*, **27**, 1215 (1935).

[16] "Tragasol Products and Their Uses," Tragasol Products, Ltd., Hooton, Wirral, Cheshire, England; E. A. Hauser, U. S. patent 1,831,492 (1931); Rhodes and Segar, *J. Rubber Res. Inst. Malaya*, **6**, 140 (1935); British patents 430,935 (1934); 336,269 (1929).

[17] Nishida and Hashima, *J. Dept. Agr. Kyushu Imp. Univ.*, **2**, 277 (1930); A. Engler, "Das Pflanzenreich," Leipzig, **1911**; IV, 23c; *Mededeelingen Afd. Handelsm. Koloniaal Inst. Amsterdam*, **8**, 177 (1929); **13**, 157 (1932); **15**, 138 (1934).

[18] Kraay, *Bergcultures*, **7**, 1124 (1933); Dutch patent 37,288 (1935); British patent 448,245 (1934).

[19] H. Staudinger, "Die Hochmolekularen Organischen Verbindungen," Berlin, **1932**, 333, 339; Dutch patent 40,075 (1937).

[20] British patents 448,203, 448,244 (1934); U. S. patents 1,775,379 (1930); 1,994,328 (1933); British patent 437,758 (1934); French patent 791,160 (1934); Dutch patents 68,286 (1936); 72,075, 75,603, 75,644, 79,507, 79,508, 79,650 (1937).

[21] Tylose S-400 of A. G. Kalle & Co., Wiesbaden-Biebrich; Sponsel, *Melliand Textilber.*, **18**, 100 (1937).

[22] U. S. patent 1,989,241 (1933); British patent 417,162 (1933).

[23] Sauer and Sanzenbacher, *Kolloid-Z.*, **79**, 58 (1937); German patent 560,259 (1932); U. S. patent 1,647,805 (1926); Dutch patent 21,247 (1927); British patent 268,299 (1927).

[24] Kraay, *Bergcultures*, **7**, 1124 (1933); Dutch patent 37,288 (1935); British patent 448,245 (1934).

[25] Dutch patent 40,075 (1937).

[26] Rahn, *Forsch. Geb. Milchwirtschaft*, **1**, 133 (1921); *Kolloid-Z.*, **30**, 110 (1922); W. van Dam, "Opstellen over moderne Zuivelchemie," **1922**, 169; van Dam, Sirks, and van der Burg, *Verslag Onderz. Rijks-Landbouwproefstat*, **26**, 106 (1922); Troy and Sharp, *J. Dairy Sci.*, **11**, 189 (1928).

[27] Baker, *India-Rubber J.*, **93**, 14 (1937); *Trans. Inst. Rubber Ind.*, **13**, 70 (1937).

[28] McGavack, *Ind. Eng. Chem.*, **27**, 894 (1935); Boggs and Blake, *Ind. Eng. Chem.*, **28**, 1200 (1936).

[29] U. S. patent 1,772,752 (1930); Dutch patent 28,801 (1932).

[30] Rahn, *Forsch. Geb. Milchwirtsch.*, **1**, 33 (1921); *Kolloid-Z.*, **30**, 110 (1922).

[31] van Dam, Sirks, and van der Burg, *Verslag Onderz. Rijks-Landbouwproefstat*, **26**, 106 (1922).

[32] Troy and Sharp, *J. Dairy Sci.*, **11**, 189 (1928).

[33] Kieferle and Sonnleiter, *Deut. Molkerei-Ztg.* (Kempten), **55**, 2 (1934).

[34] Ziegelmayer, *Deut. Molkerei-Ztg.* (Kempten), **48**, 495 (1934); *Kolloid-Z.*, **70**, 211 (1935); **71**, 214 (1935); Drewes, *Deut. Molkerei-Ztg.* (Hildesheim), **49**, 421 (1935).

[35] Kruyt and Lier, *Kolloidchem. Beih.*, **28**, 408 (1929).

[36] Kraay, *Arch. Rubbercultuur*, **21**, 16 (1937).

[37] W. Clayton, "The Theory of Emulsions," London, **1935**, 3rd Ed., 108, 246.

[38] Tiebackx, *Kolloid-Z.*, **8**, 198 (1911); **9**, 61 (1911); **11**, 102 (1922); *Pharm. Weekblad*, **59**, 574, 1014 (1922).

[39] de Jong, *Rec. trav. chim.*, **53**, 163 (1934); "La Coacervation," Paris, **1936**, I and II.

[40] Beyerinck, *Kolloid-Z.*, **7**, 16 (1910).

[41] Ostwald and Hertel, *Kolloid-Z.*, **47**, 258, 357 (1929); Ziegelmayer, *Kolloid-Z.*, **71**, 228 (1935).

[42] J. Duclaux, "Rigidite, Thixotropie et Coacervation." Paris, **1934**, 31.

[Reprinted from the India Rubber World, Vol. 98, No. 4, pages 31–33, and 38, July 1, 1938.]

Stability of Ficus Elastica Latex

F. K. Daniel, H. Freundlich, and K. Söllner

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE, LONDON, ENGLAND

Thanks to the kind endeavors of E. Hoyle (Revertex, Ltd.) of Rengam Estate and to the support given by Mr. Simpson, manager of Rim Estate, we obtained a sample of 2.7 liters of *Ficus elastica* latex. The latex had been collected at Rim Estate, Malacca, on two successive days from about 10 trees which had not been tapped since 1912. Ammonia was added to the latex in such a quantity that about 700 milliequivalents per liter of free ammonia were present; methyl red was used as the indicator. The dry matter (T. S.) and dry rubber content (D. R. C.) estimations were T. S. = 38.8 per cent, D. R. C. = 36.5 per cent.

Stability of Fresh and Preserved Latex

In his report attached to the sample Mr. Hoyle writes: " . . . we used the 'Herringbone' tapping to obtain the latex as quickly as possible. Latex oozed on to the tapping cut freely at first, for a minute or two, but quickly thickened and became apparently half coagulated. Addition of ammonia solution to the tapping cuts did not help the flow appreciably, but addition of ammonia to the latex in the cups during dripping of the trees greatly reduced the viscosity of the latex and minimized the amount of coagulum to be strained off. *Hevea brasiliensis* trees which have been resting for some months, or which are freshly opened up, also yield only a small quantity of highly viscous latex at first. With the *Ficus elastica* trees, the cuts made on November 1, 1935, were reopened the next day, but the flow of the latex was then, if anything, worse than on the first day. . . ."

This means that the latex is very unstable at the time it leaves the tree, and that this is so, regardless of the time interval between tappings.

We confirmed statements in the literature[1] that this latex when containing ammonia is very stable; when testing our sample seven weeks after tapping we found that it no longer had a tendency to be coagulated, either spontaneously or by the addition of other substances; on the contrary, it was very difficult to coagulate at all, the addition of electrolytes causing only microscopic aggregation and creaming. The cream readily redispersed on shaking.

Improvement of Stability upon Aging

From this peculiar change we must conclude that a protecting substance had been formed within the latex after tapping. From a study of Hevea and Jelutong latex we know that important changes can take place in the latex outside of the tree, and as a rule a decrease in stability is observed. The increase in stability occurring in *Ficus* latex was not due to a change of the rubber hydrocarbon as in the case of Jelutong latex, for the quantity and the quality of the *Ficus* rubber were absolutely unchanged after ten months. A change in the resins, which are present in the latex to a noticeable amount, appears to be the most probable explanation; also this change was very likely due to the NH_3 added.

Two reactions of the NH_3 may be foreseen. It may neutralize instantaneously the resinic acids which are present in the freshly tapped latex, forming resin soaps; or it may slowly saponify to a further extent the resin esters, which may constitute

the largest part of the resins in *Ficus* latex. The first reaction would account for the improved stability of the latex after addition of NH_3. It is not sufficient, however, to explain why in course of time the latex becomes so stable that it does not return to its original instability when it is acidified. In the case of the second reaction the derivatives of resin esters, produced by the saponification of higher esters, are probably capable of exercising a protecting action, even in an acid medium.

We may see a confirmation of this assumption in the fact that the reactions going on in the latex occur without consumption of oxygen, but with consumption of considerable amounts of NH_3. This is in contrast to the reaction going on in Jelutong latex, which we found to be an enzymatic process of oxidation.[2]

Reduction in NH_3 Content

Experiments were conducted to determine the consumption of NH_3 in *Ficus* latex. The NH_3 content of undiluted *Ficus* latex previously sealed in airtight containers was determined by neutralizing with normal HCl, using methyl red as an indicator. The NH_3 content decreased from 700 to only 360 milliequivalents per liter after three months. The effect of elevated temperatures on the rate of NH_3 consumption was also determined. Three carefully sealed test tubes containing latex diluted with water in the ratio of one to two were held for 12 days at different temperatures: room temperature, 40° and about 90° C., respectively; the NH_3 content was then determined. The room temperature sample required about 320 milliequivalents per liter of HCl to be neutralized; the 40° C. sample, about 280; and the 90° C. sample, 230. The results of this experiment suggest that we are dealing with a purely chemical reaction: if bacteria or enzymes were involved in the process, we ought to find a decrease in the consumption of NH_3 at 90° C. Obviously then the reaction is not due to an enzymatic process of oxidation similar to the one occurring in Jelutong latex.

Behavior upon Neutralization

If alkaline *Ficus* latex is neutralized with acid, *i. e.*, if its particles are discharged, aggregates are formed which cream quickly. Referring to the last-mentioned experiment above, the sample held at room temperature creamed most quickly and completely; the 40° C. sample creamed only partly, the creaming process requiring more time than in the first case; the 90° C. sample behaved like the 40° C. sample, but to a more pronounced degree. This apparently proves that increased saponification really causes increased protection of the particles; this implies that the protecting action is produced by substances formed during the reaction.

From a qualitative point of view there is no objection to assuming that NH_3 reacts by neutralizing resinic acids and saponifying resin esters, but from a quantitative point of view it appears unlikely that such a large quantity of NH_3 (nearly 400 milliequivalents per liter) should be consumed by these reactions alone. There are probably other reactions proceeding at the same time; for instance, the breaking up of sugars present in the latex. It is known from a study of *Hevea* latex that large amounts of NH_3 are consumed by the splitting of sugars in the alkaline medium. Furthermore, alkaline solutions of pure sugar, held in an atmosphere where the oxygen is not renewed, turn yellow and brown in course of time,[3] as did the serum of our *Ficus* latex.

Nature of *Ficus* Latex Particles

Like the resins in the *Hevea* species investigated by Frey-Wyssling[4] and unlike those of Jelutong latex,[2] the bulk of the resins in *Ficus* latex appears to be present

HEVEA BRASILIENSIS	ABIARANA GUTTA-PERCHA	FICUS ELASTICA	JELUTONG
Latex Stability			
Is coagulated spontaneously in a few hours without preservatives. Even with NH_3 the stability is only limited.	Stable without preservatives for many months. Stability not altered despite the fact that other substances in the serum are decomposed in course of time, causing the latex to become acid.	Highly unstable when leaving the tree. Very stable after NH_3 is added.	Unstable without preservatives. Very stable if alkali has been added.
Stabilizing Agents			
Proteins are most probably the substance responsible for the stability and other colloidal properties. The latex behaves like a protein suspension.	Natural stabilizing substance is distributed between the serum and the particles in a reversible adsorption equilibrium. May be washed out, and stabilizes, for instance, *Hevea* latex when added to it.	Protecting agent is adsorbed irreversibly, it cannot be washed out, and does not protect unstable latices, as the substance in *Abiarana* does. Resins are an important foreign substance. They presumably form the stabilizing agent when reacting with NH_3.	Behavior similar to that of *Ficus*, except that it is not equally stable. Chemical nature of protecting substance unknown; it is destroyed probably when reacting with H_2O_2.
Behavior towards Electrolytes			
Is coagulated readily to a lump of rubber when electrolytes are added.	Is not coagulated when electrolytes are added; the particles only cream and are redispersed on shaking.	Behaves like *Abiarana*.	Is coagulated in about 24 hours when electrolytes are added.
Behavior towards H_2O_2 and Boiling			
Is not coagulated on being boiled or by H_2O_2.	Behaves like *Hevea*.	Is coagulated on being boiled, but not by H_2O_2.	Is coagulated on boiling only if H_2O_2 has been added.
Behavior under Influence of an Electric Current			
Particles deposited by an electric current on the anode form a coherent skin.	Particles deposited by an electric current on the anode form a thin layer which can easily be redispersed.	Particles deposited by the electric current on the anode form a layer thicker than in the case of *Abiarana*, which can be redispersed by a jet of water.	Particles are partly deposited on the anode by an electric current; they do not form a coherent skin, but sticky little lumps.

Ampholytic Behavior			
Ampholytic system: Isoelectric point about p_H—4.8. Ampholytic behavior due to proteins.	Ampholytic system: Isoelectric point about p_H—4.3. Ampholytic behavior probably due to a protecting agent, which is very likely a glucoside of high molecular weight.	System not ampholytic.	System not ampholytic.
Density of Particles and Coagulum			
Particles and coagulum are lighter than the serum; they cream.	Particles and coagulum are lighter than the serum; they cream.	Particles all cream, but they are fractionated to a certain extent to a lighter and heavier layer.	Particles and coagulum are heavier than the serum. They both settle down.
Particle Types			
Small percentage of resinous particles is to be seen independent of the rubber particles.		Two types of particles: lighter particles containing more rubber, and heavier particles containing more resinous matter.	Only one type of particles Each particle contains both rubber and resinous substance. Resins are present in excess (20% against 5% rubber).
Decomposition Reactions			
		When interacting with light or air or both, the latex soon turns pink. H_2O_2 decolorizes it. Color perhaps due to alkaline decomposition of sugars.	Rubber is transformed in course of time into a resinous substance, if air is admitted. This decomposition appears to be an enzymatic reaction.
Emulsifying Property			
		Contains from the beginning substances which favor the emulsification of organic liquids (butyl alcohol, etc.) in the latex. The substance is probably a soap-like compound, formed by the reaction of NH_3 on the resins.	When the latex is oxidized in course of time, a substance is formed, favoring the emulsification of organic liquids, as in the case of *Ficus*. This is probably also a soap-like substance, produced by the reaction of a resinous substance with the alkali.

in the form of individual particles, clearly distinct from the rubber hydrocarbon particles. There are, in any case, two different kinds of particles present in *Ficus* latex. Creaming always produces a deep upper layer, pink in color, and a lower layer of less depth and white in color. The latter is formed much more slowly than the former, and can be observed only after the latex has creamed completely. Microscopically the particles of the two layers cannot be distinguished; both are about one micron to two microns in diameter. (Particles up to five microns mentioned in the literature[5] were not present in our sample.) By removing and drying the upper layer, a rubber skin of very good properties (nearly like those of a vulcanized *Hevea* rubber) was obtained. The lower layer treated in the same way gave a product which is hard and only slightly elastic at room temperature; at higher temperatures it becomes sticky and plastic, having the odor of the warm Jelutong resins. This product was partially soluble in warm acetone. Hence, there is little doubt that the heavier particles from the white layer consist in part of resins.

Effect of H_2O_2

According to statements in the literature,[6] *Ficus* latex is not pink, but white, when leaving the tree, and only becomes colored when exposed to light or air for some time. Mr. Hoyle observed that on adding ammonia to fresh (white) latex, the latex instantly turns yellow at the point where the ammonia is introduced. We found that old *Ficus* latex is quickly decolorized by H_2O_2, and when left in contact with it for several weeks, a part of the creamed latex particles becomes yellow. H_2O_2, however, does not destroy the substance protecting the particles of *Ficus* latex, as is the case with Jelutong latex; on heating the mixture of latex and H_2O_2 and adding acetic acid the latex was coagulated no more than in the case of a similarly treated latex without H_2O_2. At room temperature no difference in coagulation was noticed.

Properties of Protective Substance

This H_2O_2 experiment again proved that the protecting substance of *Ficus* is different from that of Jelutong latex. The experiment below showed that it is also quite different from the protective agent of *Abiarana* gutta-percha latex. When the serum of *Ficus* was added to *Hevea* latex, the latter was not found to be protected against coagulation by electrolytes as is the case when *Abiarana* serum is added to *Hevea* latex. This indicates that the *Ficus* rubber particles must have adsorbed all of the protecting substance irreversibly, or that the part not adsorbed on the particles must have been contained in the serum as a colloidal dispersion, like the rubber particles themselves. The protective substance, therefore, could not be adsorbed as a protecting layer on the *Hevea* rubber particles.

The protecting substance is, in any case, not dissolved in the serum, as is brought out below. Washing *Ficus* latex caused reversible aggregation, as in the case of the addition of electrolytes, instead of coagulation. This fact proves that the protective agent cannot be removed by washing and therefore is not water soluble.

Under the influence of an electric current, serum-free *Ficus* particles that had been suspended in water, being negatively charged (but not ampholytic like *Abiarana* and *Hevea* particles), migrated to the anode where they were deposited in the form of a layer. As this layer could be removed by a jet of water, disintegrating into single particles or small aggregates, the layer could not consist of coagulated particles. Thus *Ficus* particles differ in this respect from poorly protected rubber particles in general, such as *Hevea* and washed *Abiarana* particles which form a coherent layer or skin on the anode. Normal *Ficus* latex, in which the particles are

suspended in the serum, behave in the same way as a suspension of serum-free particles.

This behavior of *Ficus* latex is interesting also from another point of view. It shows that the adherence of latex particles to each other caused either by discharging electrolytes or by the electric current is not determined by their consistency, but primarily by the nature of their protecting substance, *i. e.*, it is related to the stability of the latex. For the soft *Ficus* particles behave in this respect exactly like the hard *Abiarana* gutta-percha particles (unwashed); whereas *Hevea* particles, the consistency of which lies between these two extremes, behave differently in this particular, owing to the fact that they are insufficiently protected.

Acknowledgment

The authors sincerely thank Revertex, Ltd., London, for its kind help.

References

[1] E. A. Hauser, "Latex" (Translated by W. J. Kelly), **1930**, pp. 47, 76.
[2] Daniel, Freundlich, and Söllner, *India Rubber World*, Feb. 1, **1938**, p. 49.
[3] Schade, *Z. physik. Chem.*, **54**, 1 (1906).
[4] Frey-Wyssling, *Medellel. Algem. Proefst. Avros*, **13**, 7 (1929).
[5] E. A. Hauser, "Latex," p. 76.

[Translated by Charles Blanc for Rubber Chemistry and Technology from Caoutchouc and Rubber (U. S. S. R.), pages 33–44, No. 1, January, 1938.]

A Colloidal and Chemical Investigation of Different Brands of Latex: Natural Latex, Jatex, Revertex, Revertex-T, and Revultex

B. A. Dogadkin and B. M. Kovarskaya

Moscow Institute of Fine Chemical Technology

INTRODUCTION

An investigation of the colloidal and chemieal properties of various brands of latex has become indispensable, since without such information it is difficult to select the proper concentrate for any particular rubber product, and to develop a rational technology for the manufacture of rubber products from latex.

In the present work the following products were investigated: Jatex, Revertex, Revertex-T, Revultex, and natural latex. A brief summary of the known characteristics of these products follows:

1. *Natural latex* is the milky sap of the *Hevea brasiliensis* tree. The sample examined was a yellowish liquid of the consistency of dilute cow cream. On standing it formed a brown deposit, which on stirring was easily dispersed again in the liquid. According to the literature this is supposedly a phosphorus-ammonium-magnesium salt discolored by the presence of traces of iron. To prevent spontaneous coagulation, it is treated with ammonia. The density of the sample was 0.935 and it contained 43.4 per cent of solids.

2. *Jatex* is separated from latex by the Utermark centrifugal process. In the factories of the Dunlop Rubber Co., Ltd., this process is carried out in De Laval special separators at speeds of 8000–9000 r. p. m. Immediately before the centrifugal separation, the latex is treated with ammonia to 0.3–0.5-per cent concentration. When 45 parts of 30 per cent latex are centrifuged, 23 parts of concentrated latex or Jatex and 22 parts of liquid serum are obtained. Complete separation of the latex globules is practically impossible, and a part of the rubber, particularly the very minute globules, as well as a substantial part of the soluble serum components (soluble proteins, resins, sugars, and mineral salts) remains in the aqueous residue. This explains the low stability of Jatex. The latter contains normally 55–60 per cent of solid substances. In commercial production, higher concentrates have not been obtained; it is generally believed that such concentrates are highly unstable. Jatex is also preserved with ammonia. The sample examined was white and of the consistency of thick cream. Its density was 0.941, and it contained 61.3% solids.

3. *Revertex* (standard) is produced by a patented process, comprising the evaporation of latex in a special cylindrical apparatus, fitted with a revolving roll for the removal of froth from the surface and a powerful ventilator for the vaporization of the generated water vapors. Since the process is carried on at 80–90° C., the latex is treated with special protective colloids of alkaline nature. The re-

sulting concentrate contains 80 per cent of solids. Revertex is exceptionally stable, probably because of the high content of protective colloids. The sample examined was yellowish white and had the consistency of cosmetic cream. It had the characteristic odor of albumins in the initial stages of decomposition. The density was 0.982 and the solid content was 72.3 per cent. Traces of sulfur were detected.

4. *Revertex-T* is produced by the Revertex Sales Co. The method of production is not given. Evidently this concentrate is prepared by the method used in the production of standard Revertex, *i. e.*, by the evaporation of latex in the presence of protective colloids. In all probability the difference consists in the nature of these protective colloids and also in the presence of ammonia as a stabilizing agent. Revertex-T is a product of lower concentration than standard Revertex. The nature of Revertex-T films before vulcanization is of interest technically. They are less adhesive than Revertex films, but more so than Jatex films, and the Revertex Sales Co. recommends Revertex-T for dipped goods. The sample examined was white, with a consistency of dairy cream. It formed no sediment, contained 61.23 per cent of dry solids, and its density was 0.936.

5. *Revultex* is vulcanized Revertex. According to the Vultex process, a definite quantity of precipitated or sublimed sulfur is added to Revertex and the mixture is heated in an autoclave at a definite temperature and pressure. After evaporation of water, Revultex gives a film possessing certain properties of a vulcanizate. The sample examined was yellowish and had the consistency of soft cosmetic cold cream. Its odor resembled that of Revertex. The density was 0.983. The content of dry solids was 70.2 per cent, the sulfur content, 5.2 per cent.

EXPERIMENTAL PART

I. Viscosity

Viscosity is an important property in the technology of rubber cements. Its importance in the commercial use of latex and its concentrates is equally great, since the weight of the layers formed in the production of dipped articles depends on the viscosity of the latex. Moreover, the viscosity determines the stability of mixtures of latex with various ingredients. The latter form suspensions with latex and then tend to precipitate according to the Stokes law, *i. e.*, at a velocity inversely proportional to the viscosity.

The influence of the velocity of flow, the concentration, the temperature, and the alkalinity on the viscosity of various types of latex was studied. The viscosity measurements were made in a cylindrical viscometer with a 3-cm. long tube. In construction it resembled the apparatus used at the Dunlop Rubber Co. and by Madge[1] in his investigations of the physicochemical properties of latex. It consisted of a jacketed nickel-plated brass cylinder 50 mm. in diameter and 12.5 mm. in height. The temperature in the water jacket was measured by a thermometer inserted through the aperture in the lid. The viscometer was provided at the bottom with a capillary tube of stainless steel 30 mm. long, with a corresponding orifice diameter. Capillaries with orifice diameters of 3.18, 4.77, and 6.35 mm. were available, and they made it possible to measure viscosities at various velocities of efflux.

1. *Relation between the Viscosity of Various Brands of Latex and the Velocity of Efflux (structural viscosity).*—Before carrying out the viscosity measurements in a viscometer, it seemed necessary to determine the limits of its applicability, *i. e.*, the limits of concentration of latex and latex products in which the effect of structural viscosity has not yet been investigated.

Since in all the measurements the pressure of efflux was the same, and only the size of the capillary diameter was varied, the problem was to determine the relation

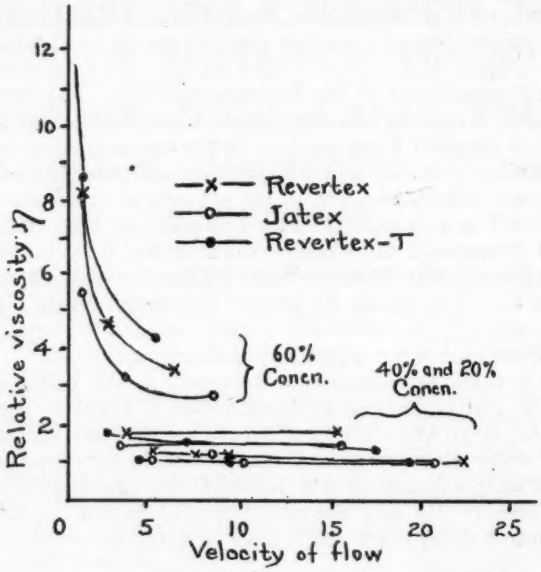


Figure 1—Influence of Velocity of Efflux on the Relative Viscosity of Various Types of Latex at Different Concentrations

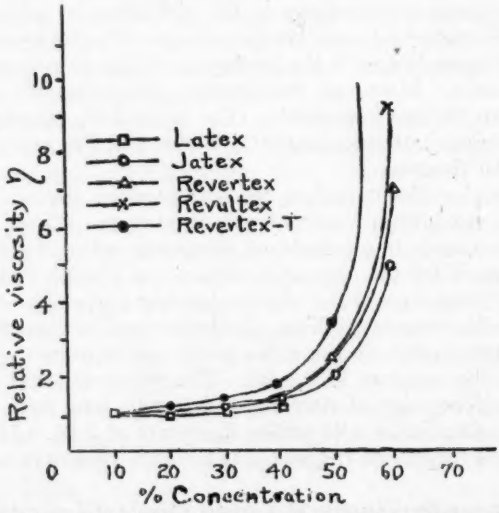


Figure 2—Relation between Relative Viscosity and Concentration

between the relative viscosity and the velocity of efflux for different concentrations of latex. This relation was studied for Jatex, Revertex, and Revertex-T at concentrations of 20, 40, and 60 per cent. In the graph (Fig. 1) the relative viscosities

are plotted as ordinates and the velocities of efflux as abscissae. The velocity of efflux is calculated by dividing the total volume of the flow liquid in cm. by the elapsed time of efflux in seconds.

The results show that the structural viscosity plays no part at concentrations up to 40 per cent, but is very pronounced for concentrations of the order of 60 per cent. The experimental data were obtained with a 3.18-mm. capillary, though at concentrations of about 40 per cent capillaries of larger inside diameters, such as 4.77 and 6.35 mm., could be used. The advantage of a slower speed of flow through a smaller capillary is that in the calculation of results the percentage error is reduced.

TABLE I

RELATION BETWEEN RELATIVE VISCOSITY AND THE CONCENTRATION OF VARIOUS BRANDS OF LATEX

Type of Latex	Relative Viscosity at Concentrations					
	10 Per Cent	20 Per Cent	30 Per Cent	40 Per Cent	50 Per Cent	60 Per Cent
Latex	1.04	1.10	1.22	1.42		
Jatex	1.05	1.09	1.25	1.54	2.25	5.02
Revertex	1.03	1.08	1.32	1.60	2.50	7.40
Revertex-T	1.09	1.19	1.43	1.91	3.50	
Revultex	1.06	1.07	1.36	1.64	2.34	9.38

2. *Relation between the Viscosity and Concentration of Various Types of Latex.*— This relation was studied at concentrations of 10–60 per cent for Jatex, Revertex, and Revultex, 50 per cent for Revertex-T, and 40 per cent for latex. The measurements of the viscosities of the original latex (concentration 72.35%), Revultex (70.2%), and Revertex-T (61.23%) by our method proved to be impossible. The data given in Table I are represented graphically in Fig. 2.

TABLE II

RELATION BETWEEN RELATIVE VISCOSITY AND TEMPERATURE FOR VARIOUS BRANDS OF LATEX OF 40-PER CENT CONCENTRATION

Brands	α	η_0 Extrapolated	Temperature 20° C. η Exptl.	20° C. η_x Calcd.	20° C. $\Delta\eta$ in %	Temperature 30° C. η Exptl.	30° C. η_x Calcd.	30° C. $\Delta\eta$ in %
Latex	0.0026	1.50	1.44	1.42	1.38	1.36	1.38	1.46
Jatex	0.0030	1.6	1.54	1.50	2.59	1.47	1.45	1.36
Revertex	0.0028	1.75	1.64	1.65	0.60	1.57	1.60	1.91
Revertex-T	0.0048	2.20	1.91	1.98	3.66	1.71	1.88	9.93
Revultex	0.0049	1.80	1.62	1.62	0.00	1.55	1.53	1.29

Brands	α	η_0 Extrapolated	Temperature 40° C. η Exptl.	40° C. η_x Calcd.	40° C. $\Delta\eta$ in %	Temperature 50° C. η Exptl.	50° C. η_x Calcd.	50° C. $\Delta\eta$ in %
Latex	0.0026	1.50	1.31	1.34	2.28	1.28	1.30	1.56
Jatex	0.0030	1.6	1.44	1.40	2.77	1.38	1.36	1.46
Revertex	0.0028	1.75	1.58	1.55	1.89	1.50	1.50	0.00
Revertex-T	0.0048	2.20	1.62	1.77	9.25	1.49	1.65	1.07
Revultex	0.0049	1.80	1.43	1.44	0.70	1.47	1.35	8.16

Brands	α	η_0 Extrapolated	Temperature 60° C. η Exptl.	60° C. η_x Calcd.	60° C. $\Delta\eta$ in %	Temperature 70° C. η Exptl.	70° C. η_x Calcd.	70° C. $\Delta\eta$ in %
Latex	0.0026	1.50	1.26	1.26	0.00	1.24	1.21	2.41
Jatex	0.0030	1.6	1.33	1.31	1.20	1.26	1.26	0.00
Revertex	0.0028	1.75	1.44	1.45	0.69	1.40	1.40	0.00
Revertex-T	0.0048	2.20	1.38	1.56	13.00	1.36	1.46	7.30
Revultex	0.0049	1.80	1.40	1.27	9.28	1.34	1.20	10.44

The curves show similar changes in viscosity with concentration for all the types of latex. Furthermore the curves cannot be expressed accurately by the Arrhenius formula $\log \eta = gAc$, where η is relative viscosity, A is a constant, and c is the concentration. Although the experimental data for concentrations of 20–50 per cent agree with this formula, the points for the concentrations of 10–60 per cent do not fall on the curve corresponding to the above formula. The results show that the relative viscosities increase in the order: latex, Jatex, Revultex, Revertex, and Revertex-T.

3. *Relation between Relative Viscosity of Various Brands of Latex and Temperature.*—This relation was studied in the temperature range of 20° to 70° C. at 40-per cent concentration for all five brands, and at 60-per cent concentration for Jatex, Revultex, and Revertex. The results are shown in Tables II and III and Fig. 3.

It is evident that, for the range of temperature examined there is a linear drop in viscosity, according to the equation:

$$\eta_t = \eta_0 (1 - \alpha t),$$

where η_t is the relative viscosity at the particular temperature, η_0 is the relative viscosity at 0° C. (obtained by extrapolation), and α is a coefficient which depends on the nature of the latex. In Table II the value η was obtained experimentally, η_x was calculated by the formula, and $\Delta\eta$ is the difference calculated in percentage.

TABLE III

RELATION BETWEEN RELATIVE VISCOSITY AND TEMPERATURE FOR VARIOUS BRANDS OF LATEX OF 60-PER CENT CONCENTRATION

Brand	Relative Viscosity at Temperature					
	20°	30°	40°	50°	60°	70°
Jatex	5.62	4.77	4.64	4.14	3.65	3.46
Revultex	7.40	6.85	6.40	5.75	4.96	4.67
Revertex	8.38	7.90	7.54	7.25	6.25	5.90

4. *Changes in the Viscosity of Various Types of Latex on Addition of Alkalies.*—These changes were studied for Jatex, Revertex, and Revertex-T at 40-per cent concentration and for Jatex and Revertex at 60-per cent concentration; various quantities of ammonia and potassium hydroxide were added. Experiments with sodium hydroxide were not continued, because on adding only 0.5 per cent sodium hydroxide to Revertex, even at 40-per cent concentration, excessive thickening took place, so that viscosity measurements were impossible. The general alkalinity of the brands of latex examined, calculated as ammonia, before the addition of reagents, was 0.73 per cent for 60 per cent Jatex, 0.35 per cent for 60 per cent Revertex, 0.48 per cent for 40 per cent Jatex, 0.23 per cent for 40 per cent Revertex, and 0.83 per cent for 40 per cent Revertex-T. In some cases the p_H values were determined to ascertain the effect of this property on viscosity.

The results show that potassium hydroxide and ammonia lower the viscosity of Jatex, Revertex, Revultex, and latex. This decrease in viscosity is particularly marked for the first 0.5 per cent of alkali. Potassium hydroxide in nearly all the cases has less effect than ammonia. The effect obtained by increasing the concentration of alkali is greater with 60 per cent than with 40 per cent latex products. Revertex-T differs in this respect from other latex products, since the addition of alkali up to 1 per cent increases the viscosity somewhat. Further addition of alkali lowers the viscosity. An explanation of this phenomenon may be found in the greater content of alkali in Revertex-T compared with other latex concentrates.

II. Stability of Various Brands of Latex

1. *Threshold of Coagulation and Threshold of Dilution.*—Latex represents a polydispersed system, composed of water, containing in true solution certain electrolytes and sugar, and a dispersed phase of particles of rubber, albuminous sub-

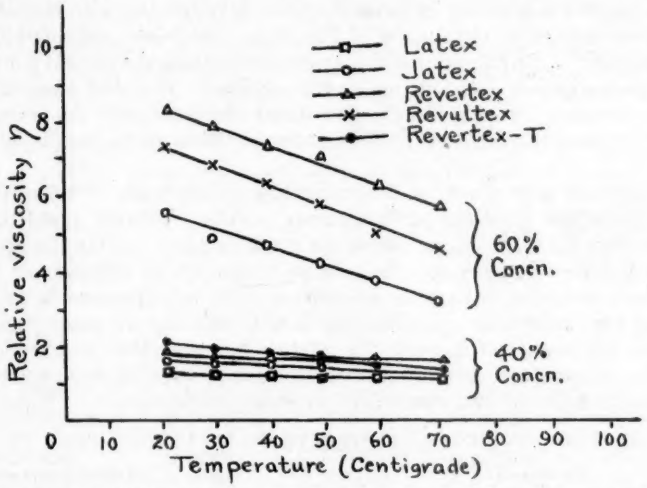


Figure 3—Relation between Relative Viscosity and Temperature for Various Brands of Latex of Different Concentrations

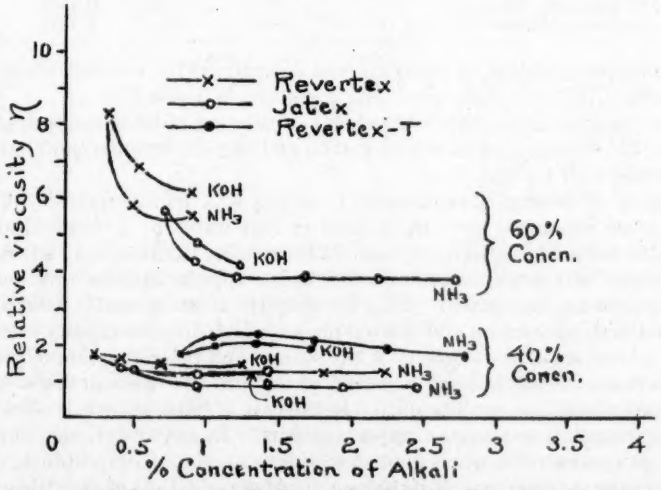


Figure 4—Influence of Alkali on the Relative Viscosity of Various Brands of Latex of Different Concentrations

stances, and resins. The latter are present in the form of a colloidal solution in the dispersed medium and partially as adsorbed films on the surface of rubber particles. The presence of an adsorbed covering on the rubber particles renders latex lyophilic and considerably influences its stability. This stability is increased by the presence

of negative charge on the globules. Spontaneous coagulation is the result of a partial denaturation of the protein envelope, which is attributable chiefly to the increasing acidity produced by fermentation. The addition of alkaline substances, such as ammonia, inhibits these processes and thereby protects against acidity and coagulation.

The electrolytic coagulation of latex is evidently connected with the adsorption of electrolyte cations on the surface of the rubber particles, resulting either in a strong depression of the potential of the latter, approaching the critical point, or in a complete neutralization of the charge on the particles. In either case coagulation takes place, because lowering the charge reduces simultaneously the degree of solvation of the protective covering and the action of the latter in stabilizing the system.

In the selection of methods of determination of thresholds of coagulation, the following procedure gave the most accurate results. Various quantities of an electrolyte from 0.1 to 1 cc. are placed on a watch glass. After the addition of water to a definite volume (1 cc.), the solution is mixed with 1–2 drops of the latex concentrate to be tested. An even distribution of the latex product in the solution shows that the electrolyte concentration is not sufficient to cause coagulation, whereas the appearance of flakes in the mixture indicates that coagulation takes place. The threshold is determined from the mean value of the two respective concentrations sufficient and insufficient to cause coagulation.

TABLE IV

Electrolyte	Molar Concentration
Ferric chloride	0.0033
Acetic acid	0.0092
Barium chloride	0.01
Magnesium chloride	0.053
Sodium chloride	1.000

The exact concentration of solutions was determined by volumetric and gravimetric analysis. The experimental data are given in Table V.

A study was also made of the thresholds of dilution of latex concentrates with soft water (12° German hardness with $CaSO_4$ and $MgSO_4$ contents) and hard water (30° hardness with $CaSO_4$).

The method of determination consists in adding to a definite quantity of a latex concentrate an increasing amount of hard or soft water to a ten-fold dilution. Observations are made immediately and 24 hours after dilution. At a definite degree of dilution of a latex concentrate fine flakes appear; further dilution causes heavy coagulum agglomeration. Thus the stability of the system is lowered with a decrease in the concentration of dispersed phase. This drop in stability is evidently related to a lowering of the viscosity of the system and the desorption of protective substances from the particles of dispersed phase into the medium (as a result of the disturbed adsorption equilibrium). In the case of hard water it is obvious that electrolytic coagulation plays an important part. In any event, the stability of latex and its concentrates when diluted is of great technical importance, and the authors consider it necessary to introduce the determination of the "threshold of dilution" as an important technical property of latex products. By the threshold of dilution is understood that minimal concentration of latex or its products which fails to produce clumps of coagulum incapable of dispersion in the medium on shaking. The greater the stability of a latex product, the lower the magnitude of the threshold of dilution. The respective behavior of various types of latex is given in Table VI.

TABLE V

THRESHOLDS OF COAGULATION OF VARIOUS LATEX CONCENTRATES IN GRAM-MOLS., PER LITER

	Initial Concentrations				
Electrolyte	Latex	Jatex	Revertex	Revultex	Revertex-T
Ferric chloride	0.00247	0.00280	0.00280	0.00181	0.00264
Acetic acid	0.00736	0.00736	0.00460	0.00322	0.00750
Barium chloride	0.00750	0.00200	0.02000	0.00150	0.00225
Magnesium chloride	0.01320	0.01320	0.01320	0.00480	0.01250
Sodium chloride	No coagulation by satd. soln.	No coagulation by satd. soln.	0.5	0.35	0.55

	45-Per Cent Concentration				
Electrolyte	Latex	Jatex	Revertex	Revultex	Revertex-T
Ferric chloride	....	0.00181	0.00148	0.00148	0.00214
Acetic acid	....	0.00460	0.00322	0.00230	0.00700
Barium chloride	....	0.00250	0.02500	0.00045	0.00225
Magnesium chloride	....	0.01590	0.01060	0.00238	0.01250
Sodium chloride	....	No coagulation by satd. soln.	0.65	0.45	0.3

	30-Per Cent Concentration				
Electrolyte	Latex	Jatex	Revertex	Revultex	Revertex-T
Ferric chloride	0.00181	0.00115	0.00032	0.00099	0.00148
Acetic acid	0.00552	0.00368	0.00230	0.00138	0.00450
Barium chloride	0.00950	0.00350	0.03500	0.00035	0.00200
Magnesium chloride	0.01680	0.01680	0.01060	0.00185	0.01500
Sodium chloride	Satd. soln. does not coagulate		0.75	0.65	0.25

	15-Per Cent Concentration				
Electrolyte	Latex	Jatex	Revertex	Revultex	Revertex-T
Ferric chloride	0.00082	0.00049	0.00049	0.00049	0.00082
Acetic acid	0.00184	0.00184	0.00138	0.00092	0.00300
Barium chloride	0.025	0.004	0.04	0.0003	0.002
Magnesium chloride	0.0265	0.0212	0.0158	0.00159	0.0175
Sodium chloride	Satd. soln. does not coagulate		1.1	1.5	0.3

The comparative data on the coagulation of various brands of latex show that natural latex has the greatest stability towards the majority of electrolytes, followed in decreasing order by Jatex, Revertex-T, Revertex, and Revultex. This order holds substantially true for the behavior on dilution with hard and soft water except for Revertex-T, which shows the minimum stability on dilution.

Coagulation in the presence of Ba ions gives somewhat different results. In this case the most stable product is Revertex. This exception can probably be explained by the formation of soluble compounds with the protective colloids of Revertex. The fact that with respect to stability towards electrolytes, Revertex occupies third place among the various types of latex is at variance with the hitherto current opinion that the greater stability of Revertex is the result of addition of protective colloids in its production. In the absence of any data in the literature on the stability of Revertex towards electrolytes it can be postulated from the method of production of Revertex that the protective colloids added to it show a maximum protective action at the temperatures used in the process, *i. e.*, 70–80° C.

The coagulating power of various electrolytes differs according to the type of

latex. The following series show the decreasing orders of coagulating power of electrolytes:

Latex: $FeCl_3$, acetic acid, $BaCl_2$, $MgCl_2$, and NaCl.
Jatex: $FeCl_3$, $BaCl_2$, acetic acid, $MgCl_2$, and NaCl.
Revertex-T: $FeCl_3$, $BaCl_2$, acetic acid, $MgCl_2$, and NaCl.
Revertex: $FeCl_3$, acetic acid, $MgCl_2$, $BaCl_2$, and NaCl.
Revultex: $BaCl_2$, $FeCl_3$, acetic acid, $MgCl_2$, and NaCl.

TABLE VI

Brands	Formation of Floccules: Content of Solids (in %) Hard Water	Formation of Floccules: Content of Solids (in %) Soft Water	Formation of Coagulum Lumps: Content of Solids (in %) Hard Water	Formation of Coagulum Lumps: Content of Solids (in %) Soft Water
Latex	43.5			
Jatex	14.85	7.43		
Revertex	17.56	8.78	8.78	
Revultex	32.6	8.1	10.9	
Revertex-T	Droplets of coagulum lumps at all concentrations		15.3	7.3

Thus in the electrolytic coagulation of various types of latex, the action of reagents conforms to the Schulze-Hardy law. Tervalent cations act more strongly than bivalent cations, and these latter more strongly than univalent cations. The only exceptions are acetic acid and barium chloride with Revertex. The peculiar effect of barium chloride on Revertex has already been mentioned.

It is of interest that coagulation of latex and Jatex does not take place even when large quantities of saturated sodium chloride are added. Likewise, latex and Jatex show the highest stability on dilution with soft and hard water. The least stable is Revertex-T, which gives minute coagulum lumps by addition of only one volume of water.

The formation of coagulum lumps on diluting with hard water takes place with Revertex at a content of 8.78 per cent of solid matter, with Revertex-T at 15.3 per cent and with Revultex at 10.9 per cent. This constitutes practical limits of dilution of these types of latex for technical application.

2. *The Stability of Latex Concentrates at Low and Elevated Temperatures.*—The problem of the stability of latices at freezing and elevated temperatures, although very important, has not as yet been dealt with in the literature. Low temperatures from −35° to −45° C. cause irreversible coagulation of some types of latex, whereas heating even up to 100° C. does not produce this effect. It is known that the freezing causes partial or complete degeneration or denaturation of protein substances, depending on the extent of freezing. Since proteins are the fundamental component of the protective layer, it is obvious that their denaturation leads to coagulation.

The method used for determining the thermal stability of latex and its concentrates was as follows. Latices in glass jars (with ground-in stoppers) were placed in a freezing apparatus at −20° and −45° C. and were kept at these temperatures for 6 and 12 hours. In tests at elevated temperatures, the samples were heated in a water bath at 60° and 100° C. Before and after exposure to the low and elevated temperatures, the samples at room temperature were tested with barium chloride, acetic acid, and sodium chloride for the thresholds of coagulation, and for their relative viscosities in a viscometer fitted with a capillary of 3.18-mm. diam.

When on freezing no irreversible coagulation took place, as with Revertex and Revultex, the resulting samples were practically indistinguishable from the untreated specimens. Irreversible coagulation was observed with Jatex at −45° C. after 6 hours, with Revertex at −45° C. after 12 hours, and with Revertex-T at −20° C. after 6 hours of exposure.

On the basis of these experimental data, it is evident that the limit of stability at low temperatures for Jatex is at slightly below −20° C., for Revertex at −45° C., and for Revertex-T at between −10° and −20° C. Revultex and latex are considerably more stable, and they showed no signs of coagulation after an exposure at −45° C. for a period of 12 hours.

When Jatex is frozen within the range of from −16° to −20° C., its viscosity increases considerably (from 1.52 to 3.26), the thresholds of coagulation become lower, and minute coagulum lumps which easily dispersed on dilution with water are formed. All these changes in Jatex indicate a condition closely related to coagulation. Under the same conditions, Revertex, Revultex, and latex do not show noticeable changes in physical and chemical properties.

It should be noted that heating at 100° C. causes an increase of viscosity in Revertex-T from 1.91 to 5.72. No other latex concentrates showed such a high increase in viscosity. The changes in other exponents are within the range of experimental error.

III. Compatibility of Latex and Its Concentrates with Compounding Ingredients

This investigation was conducted to throw light on the nature of changes in latices under the influence of the introduced ingredients. According to the literature[2, 3] powdered substances frequently coagulate latices. Evidently, fine particles of ingredients introduced into latex absorb a certain amount of moisture, and thereby increase the local concentration of latex. On the other hand, salts (electrolytes) present in the ingredients are adsorbed on the particles of rubber, with consequent reduction or complete neutralization of the charge on the particles. Lastly, it is also possible that latex proteins in the process of mixing are adsorbed at the boundary surface: water-latex (in the froth bubbles) with resulting denaturation of proteins and consquently a reduction in the stability of the system.

1. *Stability to Mechanical Action.*—In this investigation, a 250-cc. sample of latex and its concentrates, with and without the addition of ingredients, was mechanically stirred by means of a glass stirrer for various periods up to 67 hours. The ingredients used are given in Table VII.

TABLE VII

	Per Cent (Based on Rubber)
Sulfur (precipitated)	3
Zinc oxide	5
Chalk (powdered)	10
Kaolin (Turbov)	10
Carbon black (GET)	5

Since with high concentrations of the original latices measurements of the relative viscosities were impossible, the examination was limited to external changes in the products. The experimental results are given in Table VIII.

The tabulated results show that Revertex and Revultex, alone or admixed with the ingredients, are the brands of latex which are the most stable to friction by stir-

TABLE VIII

CHANGES IN LATEX AND ITS CONCENTRATES DURING STIRRING

Brands	In the Absence of Ingredients	In the Presence of $BaCl_2$ (0.001 G. Mol.)	5 Per Cent ZnO (on Rubber)	5 Per Cent Carbon Black (on Rubber)	10 Per Cent Chalk (on Rubber)	10 Per Cent Kaolin (on Rubber)	3 Per Cent Sulfur (on Rubber)
Latex	No changes after stirring for 24 and 67 hours	Appearance of 2–3 coagulum lumps after 18 hours' stirring	Formation of film on vessel walls and stirrer after 12 hours' stirring	No changes during 24 hours' stirring	Film formed on the stirrer and beaker walls after 13 hours' stirring	Small coagulum lump after 17 hours' stirring	Coagulum film after 16 hours' stirring
Jatex	No change after 24 hours' stirring; slight thickening after 67 hours' stirring	Changes identical to those of latex	Practically complete coagulation after 12 hours' stirring	No changes after 24 hours' stirring	One large coagulum lump after 13 hours' stirring	Numerous fine coagulum lumps after 3 hours' stirring; 1 large lump after 10 hours' stirring	One coagulum lump after 10 hours' stirring
Revertex	No changes after 24 hours' stirring; incipient thickening after 51 hours' stirring	No changes after 24 hours' stirring; slight thickening after 32 hours' stirring	No changes after 24 hours' stirring	No changes after 24 hours' stirring	No changes after 24 hours' stirring	No changes after 24 hours' stirring	No changes after 24 hours' stirring
Revultex	Strong thickening after 24 hours' stirring; spongy mass after 45 hours' stirring	No changes after 24 hours' stirring; slight thickening after 26 hours' stirring	No changes after 24 hours' stirring	Slight thickening after 20 hours' stirring	Thickening after 19 hours' stirring	Thickening after 16 hours' stirring	No changes after 24 hours' stirring
Revertex-T	One large lump on the stirrer after 16 hours' stirring; thickening and formation of numerous fine lumps after 20 hours' stirring		Large lump on the stirrer after 8 hours' stirring; numerous fine lumps after 16 hours' stirring	Large lump on the stirrer after 10 hours' stirring	A lump formed on the stirrer after 8 hours' stirring	A lump formed on the stirrer after 8 hours' stirring	A lump formed on the stirrer after 8 hours' stirring

ring. Revertex-T proved the least stable, giving a lumpy coagulum on stirring for 16 hours in the absence of ingredients, and on stirring for 8 hours with the ingredients. Stirring of the remaining latices in a pure state for 55–60 hours produced no change. However, the addition of only 0.001 gram-mol., of barium chloride is sufficient to cause the appearance of coagulum lumps in latex and Jatex after 18 hours of stirring, and to cause a slight thickening of Revertex and Revultex after 24 hours of stirring. The introduction of ingredients not only furthers the formation of coagulum lumps but reduces the time of stirring. Carbon black is an exception to this rule. When introduced in the amount of 5 per cent on the rubber, it caused no marked changes even after 24 hours of stirring. The changes in Jatex and Revertex-T brought about by stirring are not only more pronounced than those in latex, but take place in considerably shorter periods of time. Revertex and Revultex underwent practically no changes during 24 hours of stirring.

2. *Kinetics of the Sedimentation of Ingredients.*—The determination of the velocity of sedimentation of the ingredients in latices is important in connection with the commercial production of stable mixtures and the selection of the most suitable types of latex for any particular purpose. The velocity of sedimentation of ingredients depends on the viscosity of the latices and on the nature of the stabilizing agents present in the latices.

To determine the kinetics of sedimentation of ingredients, the latex to be tested was diluted to 30-per cent concentration, and 50 grams of solution were transferred to a measuring cylinder. After addition of the particular ingredient, the cylinder was mechanically shaken for 2 hours and then allowed to rest. The rate of sedimentation was measured by the height of the settled suspension. The percentages of ingredients given in Table IX are based on the rubber.

TABLE IX

	Per Cent		Per Cent
Sulfur (precipitated)	2	Chalk	10
Zinc oxide	5	Carbon black (GET)	5
Kaolin	10	Carbon black (Maĭkop)	5

The experimental results show that the velocity of sedimentation of any particular ingredient depends on the type of latex. In Table X the types of latex are arranged in their decreasing order of velocity of sedimentation of the ingredients.

TABLE X

Sulfur	Kaolin	Chalk	ZnO	Carbon Black (GET)	Carbon Black (Maĭkop)
Revultex	Revultex	Revultex	Revertex-T	Revertex-T	Revultex
Jatex	Revertex-T	Revertex-T	Jatex	Jatex	Revertex-T
Revertex	Latex	Revertex	Revultex	Revultex	Revertex
Latex	Jatex	Jatex	Revertex	Revertex	Latex
Revertex-T	Revertex	Latex	Latex	Latex	Jatex

Revertex and Jatex give stable suspensions of most ingredients. Suspensions in Revertex-T are less stable, though with Revertex-T precipitated sulfur gives more stable suspensions than with any other brand of latex.

SUMMARY

1. A comparative viscometric examination of various types of latex showed that:

(*a*) the viscosity of latices at a given concentration increases in the following order: latex, Jatex, Revultex, Revertex, and Revertex-T.

(*b*) the viscosity depends on the concentration of a latex, *i. e.*, the viscosity curve begins to rise sharply at a concentration of 40 per cent.

(*c*) the structural viscosity begins to play a part at concentrations above 40 per cent.

(*d*) the change of relative viscosity with increasing temperature is a linear function as expressed by the formula:

$$\eta_t = \eta_0 (1 - \alpha t).$$

(*e*) the viscosity of latices is changed by increasing the concentration of sodium hydroxide or ammonia; the most rapid decrease of viscosity is produced by the addition of the first 0.5 per cent of alkalies to Revertex and Jatex. Revertex-T under these conditions shows an increase in viscosity, the curve passing through a maximum.

2. Determinations of "thresholds of coagulation" and "thresholds of dilution" by the proposed methods showed that:

(*a*) the stability of latices towards electrolytes decreases in the order: latex, Jatex, Revertex-T, Revertex, and Revultex;

(*b*) the coagulating power of various electrolytes differs with the various types of latex (a series showing in decreasing order the coagulating power of various electrolytes for different types of latex is given on page 638);

(*c*) In agreement with the law of Schulze-Hardy, the coagulating power of electrolytes increases with increase in the valence of the cation; H ion forms an exception, since the addition of acetic acid causes coagulation at lower concentrations than do salts of bivalent cations;

(*d*) the numerical values of the thresholds of coagulation depend on the concentration of dry solids in latices; and

(*e*) dilution with hard water is possible with Revertex to 8.78 per cent of solids, with Revultex to 10.9 per cent of solids, and with latex and Jatex to any degree of dilution.

3. An examination of the stability of latices at low and elevated temperatures showed that:

(*a*) the limits of stability at low temperatures are at slightly below $-10°$ C. for Revertex-T, slightly below $-20°$ C. for Jatex, and at $-45°$ C. for Revertex.

(*b*) Revertex-T also shows the lowest stability at elevated temperatures; on heating at 100° C. considerable thickening and the appearance of coagulum lumps are observed. Other types of latex show no marked changes in physical and chemical properties on prolonged heating.

4. Experiments on mixing by stirring latices with ingredients showed that:

(*a*) Undiluted latices in the pure state are sufficiently stable in the mixing (stirring) process; and

(*b*) Revertex and Revultex are the most stable latices in the presence of ingredients; they showed no changes after 24 hours of stirring; latex, Jatex, and Revertex-T are less stable.

5. An investigation of the kinetics of sedimentation of powdered ingredients in latices showed that:

(*a*) the stabilization of various ingredients varies with different latices; and

(*b*) Revertex and Jatex give more stable suspensions with the majority of ingredients tested.

REFERENCES

[1] Madge, *Trans. Inst. Rubber Ind.*, **6**, No. 5 (1935).
[2] Hauser, "Latex," Leningrad (1932).
[3] Génin, "Chimie et Technologie du Latex de Caoutchouc," Paris, 1934.

[Translated for Rubber Chemistry and Technology from Monatshefte für Chemie, Vol. 71, No. 6, pages 444–447, May, 1938.]

The Kinetic Theory of the Elasticity of Rubber

H. Pelzer

INDUSTRIAL CHEMICAL INSTITUTE OF THE UNIVERSITY OF VIENNA, AUSTRIA

The elasticity of rubber is now realized to be analogous, not to the elasticity of a steel spring, but rather to the elasticity of a gas under compression. In other words, the elasticity is chiefly attributable, not to molecular forces, but to molecular heat motion.

This is evident most strikingly by the fact that when a steel spring under tension is warmed, its tension decreases; on the contrary, when rubber under tension is warmed, its tension usually increases. When it comes to calculations, it is best to compute the probability W as a function of the length, volume, or other parameter q, in the sense of the Boltzmann concept of entropy, by counting off the geometric possibilities of a particular state. The entropy is then:

$$S = k. \ln W(q)$$

from which the free energy:

$$F = U - TS$$

is obtained, where U represents the internal (potential) energy, *i. e.*, the molecular forces, which in the present case are of no concern.

Consequently, for isothermal changes of state, and when the internal energy plays no part, the general relation between force P and parameter q is:

$$P = -\frac{dF}{dq} = T\frac{dS}{dq}$$

This may be illustrated by the case of an ideal gas. The probability of a molecule falling within a volume V is proportional to the magnitude of the volume:

$$W = CV$$

From this it follows that:

$$F = kT \ (\ln V + \text{const.})$$

and

$$p = -\frac{dF}{dV} = \frac{kT}{V}$$

that is, the Boyle-Marriotte law, referred to 1 molecule of gas.

A strictly analogous line of reasoning applies to the elasticity of rubber, the probability of the configuration of a sufficiently large chain molecule made up of Z chain members of individual length b, being:

$$W(x, y, z)dxdydz = \text{const. } e^{-\frac{x^2 + y^2 + z^2}{2b^2z}} dxdydz$$

where the beginning of the chain is considered to be at the origin of the coördinates,

and it becomes a question of the probability that the free end of the chain is at points x, y, z, with freedom of motion dx, dy, dz.

In applying this formula to the elongation of a single chain in the direction x, it has in the past always been the rule to calculate the probability only in its dependence on the x coördinate, obtaining in the manner shown above the following expression for the tension of the chain:

$$s = kT \frac{d \ln W}{dx} = -\frac{kT}{b^2 z} x$$

i. e., an opposing force proportional to the distance between the two ends of the chain. Here the chain has zero length under no tension. To avoid this undesired result, in the present work it is assumed, without further proof, that stretching the chain in direction x is not the proper basis for calculation, but rather the dependence of the probability of the spatial absolute value L of the chain length, whereby $L^2 = x^2 + y^2 + z^2$. Accordingly the relation:

$$W(L)dL = \text{const. } L^2 e^{-\frac{L^2}{2b^2 z}} dL$$

is introduced into the method of calculation shown in the beginning, and the following expression for the free energy is obtained:

$$+F = -kT \ln W(L) = kT \left(\frac{L^2}{2b^2 z} - 2 \ln L \right) + \text{const.}$$

and from this the following expression for the tension:

$$s = +\frac{dF}{dL} = kT \left(\frac{L}{b^2 z} - \frac{2}{L} \right)$$

In this case the tension is regarded as positive if it tends to diminish L. It is evident that in this case the chain length does not become zero as the tension becomes negligible, but $L_0 = b\sqrt{2Z}$. If the relative elongation: $\frac{L - L_0}{L_0} = D$, is substituted for L, the following expression is obtained for the dependence of the tension on the relative elongation D:

$$s = \frac{\sqrt{2}k\,T}{b\sqrt{z}} \cdot D \frac{D+2}{D+1}$$

As can be seen in Fig. 1 (where the axes are changed in the usual way so that D is represented as a function of s) this reflects the character of the experimental stress-strain curve in a remarkably close manner. Moreover, according to the formula above, the initial slope of the curve would be half as great as the final asymptotic slope.

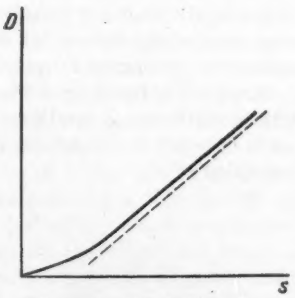


Figure 1—Elongation Curve of a Sample of Rubber, Based on Equation (1)

According to the present view, therefore, an individual chain would have the elastic properties of a macroscopic piece of rubber, in contrast to the manner of treating the

problem in the past, whereby Kuhn succeeded in deriving the ultimate length of an unstretched piece of rubber as the statistical result of the combination of many individual chains to form the total piece.

On the contrary, according to the new method, to derive the modulus of elasticity of a macroscopic piece of rubber, it is necessary only to multiply the tension of the individual chains by the number of chains, parallel to the direction of stretching, in 1 sq. cm. of cross section.

Consequently if M is the molecular weight of the structural unit of the chain, *e. g.*, isoprene, N is the Losschmidt number per mol., d is the density of the rubber, and f is the number of free rotating bonds per structural unit in the chain, then

$$\frac{fNd}{MZ}$$

is the number of chains per cu. cm., and

$$\left(\frac{fND}{MZ}\right)^{2/3}$$

is the number of chains per cu. cm. of which fraction F is in the direction of the elongation. The relation between the tension per sq. cm. and the relative elongation D of the macroscopic sample may therefore be expressed thus:

$$p = F\sqrt{2}\,\frac{kT}{bZ^{1/6}}\left(\frac{fND}{M}\right)^{2/3} D\,\frac{D+2}{D+1}$$

The elastic modulus:

$$F\sqrt{2}\,\frac{kT}{bZ^{1/6}}\left(\frac{fND}{M}\right)^{2/3}$$

obtained in this way may be compared with the experimental values.

If, for example, the absolute temperature T is 300°, b is 2×10^{-8} cm., d is 1, and M is 68, there is obtained, after dividing by 981,000 to convert dynes to kilograms, a modulus of elasticity of $1.52 \times 10^3 \frac{F}{Z^{1/6}}$ kg. per sq. cm. If this value is compared with a normal value of, for example, 5 kg. per sq. cm. for rubber, the resulting value of Z, the number of chain members between two points at which side chains of the molecular network are located, is 130 $F^{6/7}$.

Since factor F may be considerably smaller than 1, it follows that there are approximately 40 chain members between two points in the network (which moreover are not the ends of the chain, but are the points at which adjoining chains are united to the chains in question).

Since the network as a whole doubtless contributes, even if only slightly, to the kinetic elasticity, Z can be assumed to be slightly smaller. The number of isoprene units between two points in the network is, on the assumption that f is 3, equal to one-third of Z.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 14, No. 5, pages 77–79, May, 1938.]

The Behavior of Raw Rubber when Stretched Isothermally

H. Hintenberger and W. Neumann

INDUSTRIAL CHEMICAL LABORATORY OF THE UNIVERSITY OF VIENNA

Introduction

The S-shaped form of the stress-strain curve of rubber is today explained in a quite satisfactory way. In the first part of the curve, *i. e.*, the gradual ascent, work must be expended because of the van der Waals forces of attraction of the molecules; in the second part, *i. e.*, the steep ascent, the elasticity is chiefly an entropy effect, which is finally exceeded by crystallization phenomena. The phenomenon of crystallization itself has been the subject of extensive investigations, but in most cases vulcanized rubber has been employed, and because of the various accelerators and fillers which the rubber has contained, the products have been rather ill-defined. It is evident that the phenomena involved in crystallization would be much more clearly defined if the substance under investigation were to be in a higher state of purity.

If experiments are carried out with raw rubber, a flow effect is added to the various other phenomena. As a result of this flow effect, Rosbaud and Schmidt,[1] and Hauser and Rosbaud[2] as well, found that the stress-strain curve depends on the rate of elongation at very low extensions, with a greater stiffness at high rates of elongation. As found recently by Kirsch,[3] there is no evidence of any flow phenomena in vulcanized rubber at room temperature. Most investigations have been so carried out that the stress has been measured at a definite elongation. It was therefore of interest to determine the elongation at constant stress, and the changes in this relation with time and with temperature, of various types of raw rubber.

Experimental Method

Since particular importance was laid on the definite character of the substance under investigation, the first experiments were carried out with a latex which had been purified by an electrophoretic purification method developed by the Semperit A.-G., and which was kindly placed at our disposal by this company. Later in the investigation normal latex and smoked sheet also were studied.

In the experiments which are described below, strips of rubber were clamped at their ends and loaded with known weights. The elongation was followed by the change in the distance between two marks on the test-strip. Since a test-strip could be loaded only once, it was necessary to prepare the individual test-strips as nearly alike as possible, so that different test-strips showed the same behavior when treated in the same way. The latex was therefore poured on a polished, thick, flat glass plate very carefully set in a horizontal position, and from the resulting uniformly thick film (approximately 1 mm.) the individual test-strips were died out with a steel die (6 × 50 mm.).

Elongation as a Function of Time

An attempt to obtain an isothermal stress-strain curve of latex rubber failed completely because of the continued lengthening of the loaded test-specimens. If the elongation of test-specimens loaded to various extents is plotted as a function of time, a group of curves is obtained, as shown in Fig. 1. An examination of these curves will make it evident that at small loads the elongation does not have a

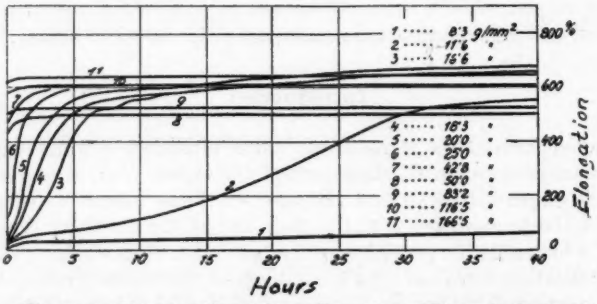


Figure 1—Change of Length as a Function of Time of a Series of Latex Rubber Samples of the Same Dimensions but Stressed under Various Loads at 20° C.

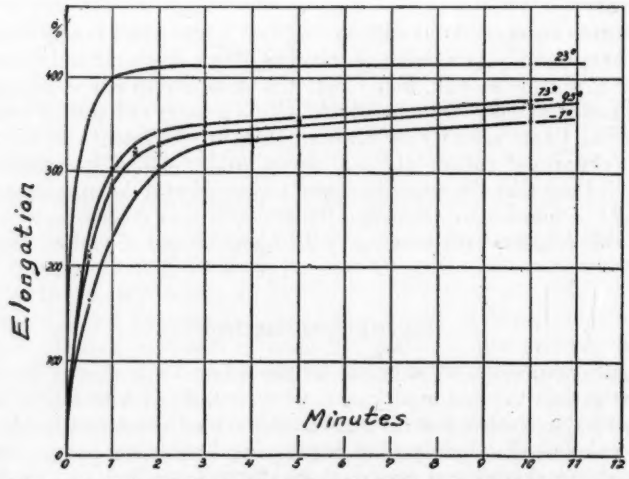


Figure 2—Rate of Elongation as a Function of the Temperature (Load of 45 Grams per Sq. Mm.)

constant value, for the curves indicate a continued increase in length, the slopes of which depend on the load, whereas at high loads (over 50 grams per sq. mm.) the curves soon reach constant values.

At a load of 45 grams per sq. mm., the rate of elongation can be measured very readily. The time-elongation relation for this load at various temperatures was plotted, as shown in Fig. 2. Within the range of temp. investigated (−1° to +23° C.) the rate of elongation increased with the temperature.

Elongation as a Function of Load

If the elongations of the variously loaded test-strips after the same length of time are plotted as a function of the load, a curve analogous to the isothermic elongation curve is obtained. As may be concluded from what has been said, the trend of this curve for short times of loading depends greatly on the duration of the loading, whereas for longer periods of loading (over 50 hours) the type of curve is different, as shown in Fig. 3. A sharp maximum is evident in the elongation values at a quite definite and at the same time relatively small load (approximately 17 grams

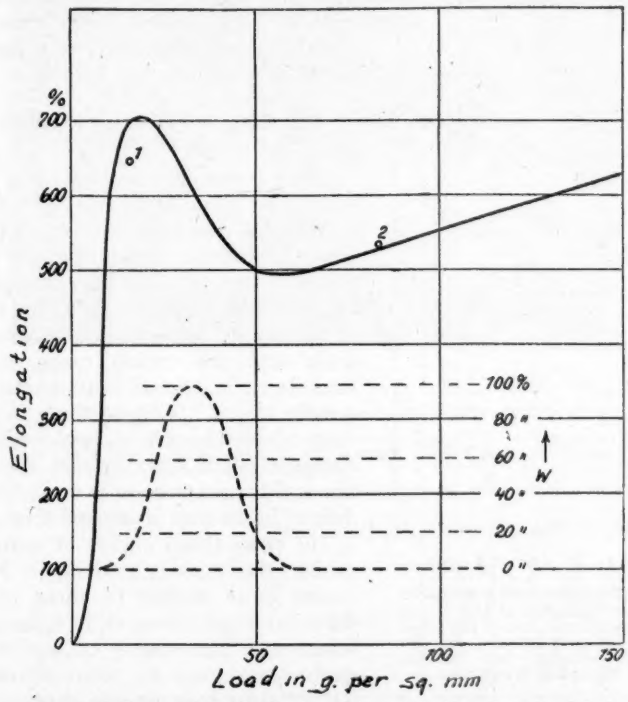


Figure 3—Elongation of a Series of Latex Rubber Samples of the Same Dimensions as a Function of the Load after Being Stressed for 50 Hours at 20° C. The Dotted Curves Represent the Probability of Tear as a Function of the Load

per sq. mm.). The higher the temperature, the more prominent is this maximum. Figure 4 shows these stress-strain curves at various temperatures.

Anomalies in the Tensile Strength

If the probability of rupture of a strip of latex rubber is plotted as a function of the load, a peculiar curve is obtained. There is a critical range of loads within which the latex strips break very frequently, whereas at lower and at higher loads they are more resistant. At very high loads they naturally break immediately, whereas rupture in the cases in question takes place only after hours. The broken curve in Fig. 3 represents the probability of rupture, W:

$$W = \frac{\text{number of broken test-specimens}}{\text{number of specimens tested}}$$

as a function of the load. It is evident that the critical range of elongation is coincident with the descending part of the stress-strain curve. The higher the temperature, the sooner the critically loaded test-specimens break, whereas at temperatures below 16° C. (with decanted latex) rupture did not take place. The x-ray diagram of a test-specimen elongated to a high degree by a small load (*e. g.*, sample no. 1 in Fig. 3, with elongation of 648 per cent, load of 16.6 g. per sq. mm., time of loading 28 hours) is shown in Fig. 5a. In this case crystal interferences are hardly recognizable. On the contrary, the picture of a highly loaded but less greatly elongated sample (*e. g.*, sample no. 2 in Fig. 3, with elongation of 530 per cent, load of 83 g. per sq. mm., time of loading 28 hours) shows strong crystal interferences, as is evident in Fig. 5b.

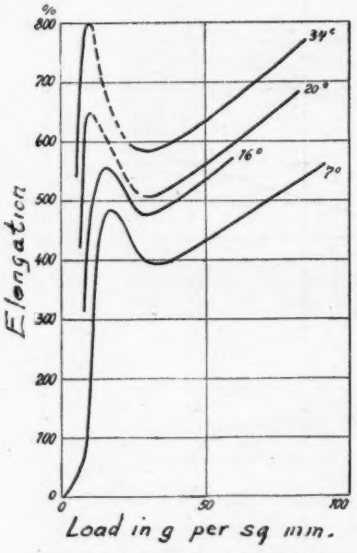


Figure 4—Elongation of a Series of Latex Rubber Samples of the Same Dimensions as a Function of the Load at Various Temperatures. In the Section Represented by Broken Curves the Samples Ruptured

The Behavior of Smoked Sheet and Normal Latex

Other types of rubber show a behavior similar to that of the latex rubber described. A stress-strain curve of smoked sheet loaded for a period of 50 hours is shown in Fig. 6. Here the elongation maximum is not clearly visible, since rupture of the samples takes place at relatively small loads and the critical range of loading extends to indefinite limits of smaller and greater loads. Whereas there is a further range above the critical load within which electrodecanted latex rubber shows resistance, this phenomenon is much less clearly defined in the case of smoked sheet.

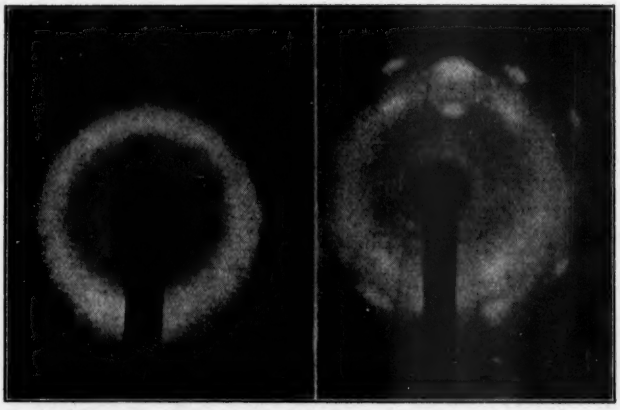
The stress-strain curves of normal latex rubber show, as is evident in Fig. 7, a course quite similar to those of electrodecanted latex; however, in spite of the unmistakable appearance of the first elongation maximum at temperatures up to 30° C., there was no case of rupture in the descending part of the elongation curve. Only at higher temperatures (above 40° C.) did anomalies in the strength become evident.

Discussion of the Results

The appearance of a maximum in the isothermal stress-strain curve can be readily explained as the combined effect of flow and crystallization phenomena. When a small load which has given a high elongation is removed, a large irreversible extension remains, whereas after the removal of a large load which has given still higher elongations, the extension is completely reversible.

If then it is assumed that crystallization commences at a definite elongation, and that the whole structure thereby stiffens, it is obvious that there must be a maximum in the curve. The x-ray photographs (Figs. 5a and 5b) support this assumption, since almost up to the maximum point, no interferences are yet visible, whereas heavily loaded samples show a distinct fiber diagram. Rosbaud and Hauser[2] likewise found that a strip of raw rubber which had been stretched very

slowly showed no crystal interferences, even at high elongations. Particularly noteworthy is the low modulus in the descending part of the stress-strain curve. In this range crystallization obviously sets in, and it appears as if this anomaly in the modulus is analogous to the relatively low modulus of a metal in proximity to its transformation point.



a b

Figure 5a—Roentgen Diagram of a Lightly Loaded, Highly Elongated Test-Strip (648% Elongation, 16.6 G. per G. per Sq. Mm. Load. Sample 1 of Figure 3

Figure 5b—Roentgen Diagram of a Heavily Loaded Less Elongated Test-Strip (530% Elongation, 83 G. per Sq. Mm. Load, 28 Hours under Stress). Sample 2 in Figure 3

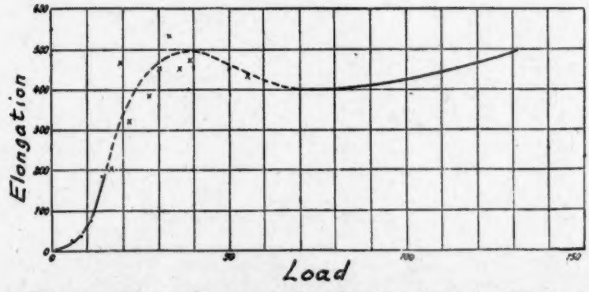


Figure 6—Elongation of a Series of Strips of Smoked Sheet of the Same Dimensions as a Function of the Load at 20° C. The Critical Range of Loading Is Broader and Less Well Defined because Decanted Latex Was Used. Marks X Represent Ruptured Test-Specimens

In the case of smoked sheet, with which the range of low moduli extends on both sides, it appears that the preliminary thermal treatment brings about partial mastication, and the relatively short chains are responsible for the particularly marked anomalies in modulus. On the contrary, with normal latex rubber, in which all resins and proteins are still present, these non-rubber components probably have a reënforcing effect, as is evidenced by the fact that the anomalies in modulus appear only at elevated temperatures.

Résumé

The elongation of raw rubber, including electrodecanted latex rubber, normal latex rubber, and smoked sheet, as a function of the stress applied and the time of this stress, was investigated in some detail. A well-defined maximum elongation was found at a quite definite relatively small stress, and accompanying this a critical range of loading within which the raw rubber broke with abnormal frequency, whereas the same rubber withstood successfully not only lower but also higher stresses.

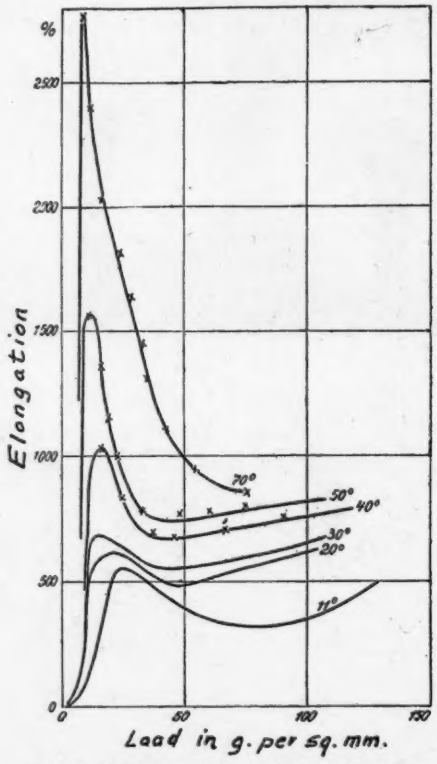


Figure 7—Elongation of a Series of Samples of Normal Latex Rubber of the Same Dimensions as a Function of the Load at Various Temperatures. Marks X Represent Ruptured Test-Specimens

Acknowledgment

The authors wish to express their appreciation at this time for the encouragement and furtherance of the work by Professor H. Mark.

References

[1] Rosbaud and Schmidt, *Z. tech. Physik*, **9**, 98 (1928).

[2] Hauser and Rosbaud, *Kautschuk*, **4**, 12 (1928).

[3] Kirsch, *Thesis*, Berlin, **1937**.

[4] These experiments were carried out by V. Hauk.

[Translated for Rubber Chemistry and Technology from Gummi-Zeitung, Vol. 52, No. 21, pages 541–542, May 27, 1938.]

The History of Rubber

Franz Carl Achard's "Experiments on Elastic Resin"

Leo Eck

DORTMUND, GERMANY

It is a curious fact that it is in the history of rubber that extreme difficulty is encountered in altering current beliefs. This is attributable in part to the fact that the history of rubber is usually treated in a cursory way in the introduction to a work, and an investigation of the original sources is ordinarily omitted. It is also attributable to the general belief that everything has been settled in this field, and therefore that it is sufficient merely to refer to this or to that original work. The present writer has plenty of evidence at his disposal to support this contention. Although of great value in its day, the compilation of scientific publications on the entire history of rubber by A. Slingervoet Ramondt[1] is today out of date in many respects. Unfortunately too, much that is of value in this work has been forgotten.

Slingervoet Ramondt[2] cites, for example, Gmelin's "Handbuch der Chemie"[3] to the effect that Achard studied the action of nitric acid on rubber. As a matter of fact the original work of Achard is not mentioned, either in any notes in the text or in the chronological list of references to the literature. The present author has therefore deemed it a pleasant task to make better known the contributions of a German chemist to the earliest investigations of rubber, a chemist whose name is already held in high esteem for his work in another field, the production of beet sugar.

Franz Carl Achard (born in Berlin on April 28, 1753, died in Breslau, April 20, 1821) published in 1777 for the first time his experiments on elastic resin,[4] and later in 1780 incorporated them in his "Chymisch-Physische Schriften." Achard's work is especially noteworthy at the present day because of the fact that it is the first investigation of that most surprising physical property of rubber, which was termed by Achard its extensibility. In addition, Achard appears to have been the first to subject rubber to dry distillation. Then again, like most of those of his day who worked with rubber, he endeavored to find a satisfactory solvent, and he studied the action of acids and of alkalies.

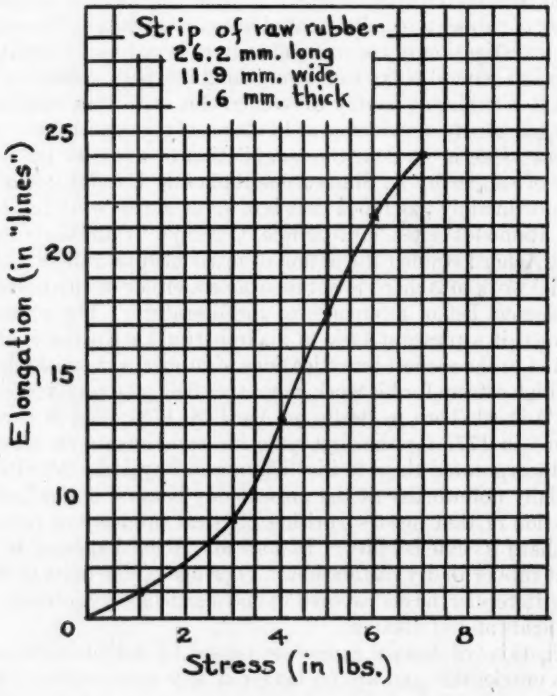
The investigations of Achard cannot be passed by with the disparaging remark that they are unscientific and are no longer of any importance. Only the unhistorically minded can speak thus, and by so doing they rightly bring upon themselves the stigma of an unscientific attitude. Untiring efforts were necessary in order to find a solvent, and they were a necessary preliminary step towards all subsequent knowledge. Then again, it is recognized today that an explanation of the constitution of rubber, and thereby the possibility of preparing it synthetically, depends to a great extent on studies of its distillation and of the products obtained. Are there not then sufficient grounds for honoring the one who, one hundred and sixty years ago, carried out the first distillation of rubber? Is any excuse necessary if adequate space is taken here for a chemist who was the first to attempt to measure the extensibility of rubber, and who discovered the regularity of the curve obtained? The insufficiency of his resources and technic does not diminish the value of his contribution.

Before describing in detail the experiments of Achard, attention should be called to another investigator, whose work also is still in the state of a "sleeping beauty,"

in spite of the fact that the work may be considered as the most profound monograph of the eighteenth century. It is that of the Dutch investigator, Arnold Juliaans.[7] However, his contributions will be reserved for a later discussion.

The Tensile Experiments of Achard

After describing briefly the origin, harvesting, properties, and use of rubber in its native countries, Achard describes his attempts "to find out to what extent this elastic resin can be expanded." To this end he pumped air into a rubber bottle having a capacity of 1.5 inch (26.96 cc.) with the expectation, after the rubber had attained its maximum expansion, of measuring its volume and thus calculating



its extensibility. However, the experiment failed, because he had no knowledge of how much pressure was to be applied.

The rubber bottle expanded greatly, became as thin as a sheet of paper, as transparent as a pig bladder, and finally burst loudly. Achard observed that the walls of the rubber flask were very uneven in thickness, and that the rubber at the thinnest points in the walls, *i. e.*, where expansion had been greatest, had lost considerable of its elasticity.

A second experiment was carried out "to determine accurately the relation between the elongation of elastic resin and the force applied to elongate it in this way." He wrote, "I fastened between two grips the two ends of a strip of elastic resin, 12 'lines' long, 5.5 'lines' wide and 0.75 'line' thick. One grip I hung vertically on an iron hook, and to the other grip, which with the strip of rubber likewise hung vertically, I attached a pan in which I could lay weights." In explanation it might

be added that the measurements given correspond to a length of 26.2 mm., a width of 11.9 mm., and a thickness of 1.6 mm., based on a "Prussian line" of 2.18 mm. The successive loads were 1, 3, 4, 5, 6, 7, and 8 pounds (the pound at that time may be assumed to have been approximately 360 grams). The elastic resin ruptured under a load of 8 pounds. The accompanying illustration with its curve gives the measurements of Achard. Although he gives only this curve in his publication, Achard believed that "it should be possible to determine, by means of an algebraic formula representing the mutual relation between the abscissae and ordinates of this line, how much a given force would elongate elastic resin."

Chemical Experiments

Achard describes about fifty experiments which he "carried out with the intention of obtaining more information on the nature of elastic resin and its behavior with various solvents." Only those experiments which are distinguished because of their novelty, or which still may be of interest for other reasons, have been chosen for discussion at this time.

First of all, Achard established the fact that after fusion rubber loses its characteristic properties and that, when incinerated, an incombustible substance (ash) is obtained. By cautious distillation of his elastic resin, he collected in the receiver a thin brown-yellow oil with odor of roast ham, while at higher temperatures a much thicker oil, with an odor as if it were badly burned, distilled. When the distillate was shaken with a couple of drops of sulfuric acid, it became as thick as balsam, gave a milky liquid with water and a clear brown solution in alcohol. Addition of an alkali caused the oil to separate again. Since the original distillate only partially dissolved in alcohol, Achard concluded that two oils are formed by distillation, one having the properties of "essential" (ethereal) oils, the other having the properties of fat oils. Whether or not this conclusion may today seem quite childish, it is nevertheless highly significant that more recent investigations have confirmed the solubility of the higher fractions in alcohol. The discovery that two different oily products are obtained by the dry distillation of rubber (this work was extended by Juliaans[8] in his fractional distillation experiments) accounts for the belief, which was held for so long, that rubber itself is a complex substance and that it should be possible to synthesize it from these components. Although on an entirely different basis, this double nature of rubber ("its modifications") is of significance even today in modern science. Naturally the inadequate technic and the impurity of the material in the early experiments must be taken into account.

A further experiment led to the highly important and, in the opinion of the present author, the original discovery that rubber goes "completely into solution" in the distillate obtained from itself (rubber oil). In this case, as elsewhere, when Achard speaks of solution he probably knew full well that this was not solution in the ordinary sense, for he did not forget to add that the solution was "greasy and very viscous." In any case, statements that Berniard in 1781 was the first to describe the oil which is formed in the dry distillation of rubber and that its ability to dissolve rubber was discovered at the beginning of the thirtieth year of the past century[9] should be corrected.

By treatment of the distillate with dilute nitric acid, Achard obtained a yellow resin, having a melting point of 100°; on the other hand, with hydrochloric acid he found that a noticeable thickening (polymerization ?) took place.

The elastic resin itself was converted by sulfuric acid, into a black, greasy mass, with the odor of sulfur dioxide, which, freed of sulfuric acid by addition of water, was insoluble in alkalies. Hydrochloric acid had almost no effect on it, and did not change its elastic properties. Concentrated nitric acid attacked it only on the

surface, with formation of a yellow, brittle crust, and did not damage the elasticity of the mass within. Fuming nitric acid dissolved the rubber, with effervescence and evolution of heat, and formation of a transparent dark brown liquid, which became turbid on addition of water and deposited a yellow flocculent mass. After washing and drying, this nitrated product was soluble in alcohol, in all acids, and in alkalies, and ignited even at 100° C.

The elastic resin of Achard was not attacked by alkalies, in fact he found that the elasticity increased slightly. Ammonia had a less favorable effect.

In continuation of the experiments of Macquer on solutions in ether,[10] Achard tested the "solvent power" of the ether "which was obtained from hydrogen chloride," of ether nitri and of the ether of acetic acid. These ethers, which are today more correctly termed esters, were at that time more or less impure as a result of their imperfect methods of preparation. Thus the first one, called also ether chloratus, ether chloricus, chloroether, and heavy muriatic ether, was even in the time of Liebig[11] composed of a mixture of "chloral and chlorine derivatives of acetal and of ethyl." According to Achard, only the last of these dissolved his elastic resin completely and left the resin "as elastic as ever," after evaporation of the solution.

Not less than twenty-five different oils were tested by Achard for their ability to dissolve rubber, as a result of which experiments certain facts were established. In the words of Achard "it is evident from these experiments with various oils:

1. That almost all essential oils have a solvent action on elastic resin, but that there are great differences, not only in the readiness with which solution takes place, but also in the proportions of the various oils in which the elastic resin dissolves. Camomile oil, oil of turpentine, and oil of amber had the most rapid and strongest solvent action.
2. That fat oils had only a relatively slight action on elastic resin. Among all the oils of this kind which were tested, sweet almond oil was the one which attacked elastic resin most severely.
3. That empyreumatic oils have a more pronounced action on elastic resin and dissolve more of it than do fat oils, but have less action than do essential oils."

The experiments of Achard with solvents also led to a practical application, *viz.*, his proposal to manufacture surgical and other goods, which up to his time had been made by the expensive Macquer ether process,[10] by the precipitation process which had been worked out by himself. In this process the more or less tough, mucilaginous, and therefore plastic rubber which was obtained by precipitation from its solutions by alcohol was molded into the desired form and then exposed in the open air and thus dried. According to Achard, rubber treated in this way recovered its "consistency and resiliency."

To summarize briefly, Achard carried out the first experiments on the stress-strain properties of rubber; subjected it to dry distillation; discovered that rubber is soluble in its own distillate; found other suitable solvents, among them ethyl chloride; studied the action of various acids and alkalies on rubber; observed the thickening (polymerization ?) which takes place in its distillate; and finally proposed a cheap process for the manufacture of surgical goods, based on the conversion of rubber to a plastic condition whereby it can be molded into various shapes.

References

[1] "Zur Geschichte der Kautschukforschung," Dresden, 1907.

[2] A. Slingervoet Ramondt, "Zur Geschichte der Kautschuk," p. 29.

[3] Gmelin, "Handbuch der Chemie," 1866, 7, II, 1763 (this source of information is taken directly from Slingervoet Ramondt).

[4] Franz Carl Achard, "Beschäftigungen der Berlinischen Gesellschaft Naturforschender Freunde," III, 356.

[5] Franz Carl Achard, "Chymisch-Physische Schriften," Berlin, 1780, by Arnold Wever.

[6] Mention should be made here of Himly, who was probably the first to obtain isoprene; cf. his *Thesis*, Göttingen, 1835.

[7] Arnold Juliaans, "Arnoldi Juliaans Rheno-Trajectini Dissertatio Chemica de Resina Elastica Cajennensi MDCCLXXX (1780), Trajecti ad Rhenum (Utrecht) defensa."

[8] *Ibid.*, p. 23.

[9] Barnard, English patent 6466 (1833) on a "hitherto unknown solvent."

[10] In the opinion of the present author, the priority always accorded heretofore to Macquer needs to be corrected.

[11] Hermann Hager, "Handbuch der Pharmaceutischen Praxis," Springer, Berlin, 1887, I, 179.

[Translated for Rubber Chemistry and Technology from Naturwissenschaften, Vol. 26, No. 13, pages 199–200, April 1, 1938.]

The Fusion Curves of Rubber and Gutta-Percha

Kurt H. Meyer

LABORATORIES OF INORGANIC AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF GENEVA, SWITZERLAND

It is already known that many rubber-like substances such as elastic sulfur and polyphosphornitryl chloride show crystal interferences when stretched, and that these interferences disappear again when the tension is removed. This shows that the melting point is increased by traction, and von Susich[1] actually determined roentgenographically the relation between the melting point and deformation and thus obtained a "fusion curve."

This phenomenon can be explained by means of the kinetic theory of the elasticity of rubber.[2] According to this theory, the stress set up in rubber when stretched depends on the fact that heat motion tends to restore to the statistically favorable, crooked, and hence shorter form, the primary valence chains which have been extended by traction and thus are in a statistically less probable position and form. For, as a result of free rotation, it is possible to have many curved forms but only one maximum elongated form; the thermodynamic probability β, and on account of the relation: $S = R \ln \beta$, the entropy S as well, are consequently greater in the unstretched than in the stretched state.[3]

At the melting point, the relation:

$$E_{am} - E_{crys} = T(S_{am} - S_{crys})$$

holds true, where E_{am} is the energy in the amorphous state and E_{crys} is the energy in the crystalline state.

Since when the rubber is elongated, S_{am} is smaller than it is when the rubber is in the unstretched state, S_{am} S_{crys} is likewise smaller; furthermore since the heat of fusion $E_{am}-E_{crys}$ depends to only a small extent on the temperature, T must increase as soon as $S_{am}-S_{crys}$ becomes smaller.

Quantitatively the following cyclical process takes place. A sample of rubber which is crystalline in the stretched state and is under a stress, K, fuses just above its melting point T, thereby absorbs heat of fusion λ, and contracts a distance l, so that the work performed is lK. When the rubber is then cooled to a temperature $T-\Delta T$ just below the melting point, and in this way crystallization is again brought about, work $(K - \Delta K)l$ is expended, and heat of crystallization λ is liberated. The work produced is therefore $lK-(K-\Delta K)l=l\Delta K$. On the basis of the second fundamental law:

$$\lambda = T \frac{ldK}{dT}$$

Gutta-percha is particularly suitable as an experimental material because of its rapid crystallization. Naturally slightly vulcanized gutta-percha should be em-

ployed to avoid permanent set, which in the case of unvulcanized gutta-percha makes it impossible to work under reversible conditions. Gutta-percha stretched to a maximum and thus crystallized so that it was in a state of complete phase orientation was warmed under various loads. Under these conditions the melting point was easily recognizable at the beginning of the contraction and could be determined with a precision of 1° C.

Figure 1 shows the fusion curve,[5] and in the table the contraction of a gutta-percha thread and the corresponding loads are recorded.

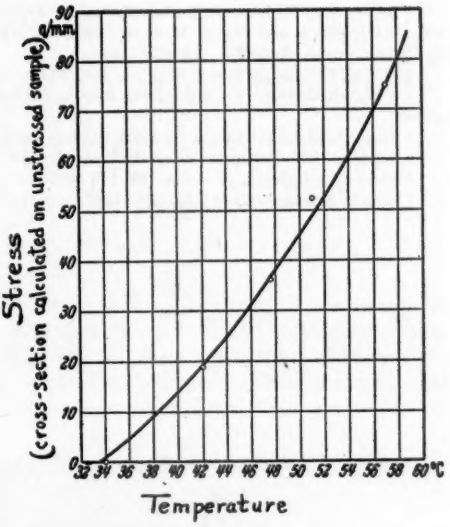


Figure 1—Melting Point of Gutta-Percha as a Function of Stress

The heat of fusion of gutta-percha is 8 ± 2 calories per gram, a value which is close to that for rubber, which Hock[6] found to be 7 calories per gram by direct measurement of the heat of extension.

TABLE I

CONTRACTION DURING FUSION OF GUTTA-PERCHA THREAD LOADED TO VARIOUS DEGREES

(Length unstretched 1 cm., cross section 1 sq. mm., maximum length stretched 5.5 cm.)

Load (Grams per Sq. Mm. of Cross Section of the Unstretched Sample)	Contraction (in Cm.)	Temperature of Fusion
0	4.5	34° C.
19	4.03	41
36	3.67	47.5
54	3.04	51
84	..	57

Since rubber, like gutta-percha, has a greater density in the crystallized state than in the amorphous state, the melting point must also increase when the pressure increases. The density of crystallized rubber as determined roentgenographically[7] is 1.02; the density of amorphous rubber is approximately 0.94. Based on these values and the heat of fusion of approximately 7 calories per gram, the calculated increase in the melting point is approximately 0.09° C. per atmosphere increase in pressure. As recently shown by Kirsch,[8] the temperature at which crystallization commences is increased by an increase in pressure.

References

[1] von Susich, *Naturwissenschaften*, **18**, 915 (1930). See also Thiessen and Willstadt, *Z. physik. Chem.*, **29B**, 359 (1935).

[2] Meyer, von Susich, and Valko, *Kolloid-Z.*, **59**, 208 (1932). See also Busse, *J. Phys. Chem.*, **34**, 2870 (1932); Guth and Mark, *Monatsh.*, **69**, 93 (1934); Meyer and Ferri, *Helvetica chim. acta*, **18**, 570 (1935); Kuhn, *Kolloid-Z.*, **76**, 258 (1936).

[3] Meyer, *IX^e Congr. intern. chim.*, **4**, 130 (1934).

[4] Our sincere thanks are due A. van Rossem for furnishing a sample of suitably vulcanized gutta-percha.

[5] Strictly speaking, there is no sharp melting point but a "fusion range" of about 2° C.

[6] Hock in "Handbuch der Kautschukwissenschaft" by Memmler, p. 489.

[7] Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936).

[8] Kirsch, *Z. angew. Chem.*, **50**, 964 (1937).

[Translated for Rubber Chemistry and Technology from Naturwissenschaften, Vol. 26, No. 8, page 123, February 25, 1938.]

A New Transformation Product of Rubber

O. Kratky, H. Philipp, K. W. Posnansky, and F. Schössberger

Industrial Chemical Institute of the University of Vienna, Austria

As investigations carried out long ago have shown,[1] rubber reduces silver nitrate. On the contrary, experiments with specially purified unvulcanized rubber films have shown that the rubber itself is not the reducing agent, but rather impurities in the non-rubber components; in fact, it is even possible to incorporate large quantities (up to about 20 per cent by weight) of silver nitrate in rubber. In

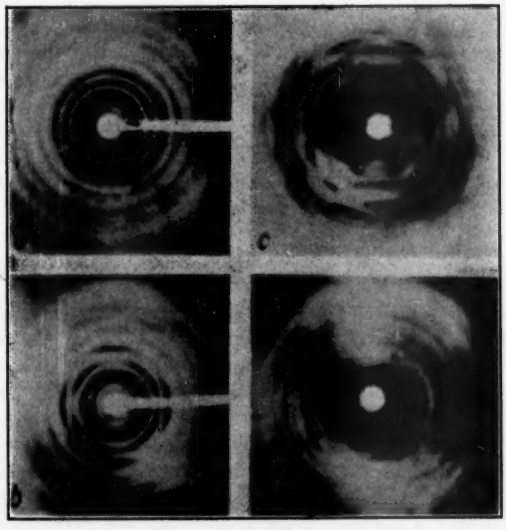


Figure 1

the experiments to be described, rubber films were prepared by drying latex which had been electrodecanted repeatedly; these films were swollen in a solution of silver nitrate in a mixture of water and acetone, and were then dried. The films obtained in this way were noteworthy for their high tensile strength compared with the original films, and were studied by means of x-rays. Instead of the diffused ring which appears ordinarily when unstretched rubber is examined, the x-ray diagram of this new product showed a series of sharp rings (see Fig. 1a) which did not correspond to any of those of inorganic silver compounds. When the product was stretched, the diagram changed, without appreciable alteration of the glancing angle, into that shown in Fig. 1b and finally into that shown in Fig. 1c. Figure 1c also shows a fiber diagram different from that of ordinary stretched rubber.

With irradiation parallel to the plane of the film of rubber, the x-ray diagram shown in Fig. 1d is obtained. This is different from that shown in Fig 1c. Accordingly, as in the case of ordinary rubber,[2] a more highly oriented fiber structure is formed, so that the sharpness of many of the reflections in Fig. 1d are surprising. Either a new modification of rubber or a chemical transformation product, probably in the sense of a permutoid reaction, is concerned in the phenomena just described. The spontaneous crystallization which takes place even in the unstretched state is worthy of note. An x-ray evaluation of the new product and a description of its physical and chemical properties are the subjects of further investigation, and will be published in detail within a short time.

References

[1] Fischer, *Kastn. Arch.*, **9**, 343.
[2] Mark and von Susich, *Kolloid-Z.*, **46**, 11 (1928).

[Reprinted from Industrial and Engineering Chemistry, Vol. 30, pages 1031–1036, September, 1938.]

Colloidal Structure of Rubber in Solution

Effect of Precipitants*

S. D. Gehman and J. E. Field

The Goodyear Tire & Rubber Company, Akron, Ohio

RUBBER solutions are somewhat unstable and their colloidal structure, usually characterized by viscosity, can be influenced by a large number of agencies such as light, oxygen, and small amounts of various reagents. The colloidal changes caused by the addition to a rubber solution of typical nonsolvents or precipitants, such as alcohol or acetone, are distinguished by the fact that they are reversible. If the precipitant is removed, the original solution can be recovered. The reversible colloidal changes, which result eventually in precipitation, were studied in the work here reported as a means for acquiring knowledge of the colloidal structure of rubber in solution. As in a former article (*8*) an effort is made to utilize comparatively recent advances in the general theory of the liquid state (*3*, *5*, *9*).

Previous publications dealing with the effects of nonsolvents on rubber solutions have been predominantly of technical interest and limited almost exclusively to viscosity measurements. LeBlanc and Kröger (*13*), Messenger and Porritt (*2*, *15*), Kawamura and Tanaka (*11*) described the viscosity changes which ensue upon the addition of various nonsolvents to rubber solutions. Whitby (*25*) classified the reagents which can be used to affect the viscosity of rubber solutions. In a later publication (*23*) he discussed an interesting experiment during which incipient precipitation was observed with the ultramicroscope. Lens (*14*) reported the results of a few measurements of the effect of alcohols on the relative intensity of the light transversely scattered by benzene solutions of rubber. Ford (*6*) and Fabritziev, Buiko, and Pakhomova (*4*) studied the modification of technical rubber cements by the use of nonsolvents. The colloidal effects of precipitants on solutions of high polymers such as polystyrene have been observed and are of interest in connection with this work (*18*, *21*, *22*, *26*).

Apparatus and Methods

This study of the colloidal changes caused by the addition of precipitants to rubber solutions was carried out by means

*For the first paper in this series, see literature citation (*8*).

of viscosity measurements and measurements of the intensity and depolarization of the transversely scattered light, employing the apparatus, technic, and theoretical analysis which were previously described in detail (*8*).

Pale crepe rubber purified by acetone extraction and diffusion in petroleum ether was used (*1*). Midgley and Henne (*16*) recently criticized the process of diffusion for the separation of sol and gel rubber, basing their conclusions on the results of an experiment in which ethyl ether was the solvent.

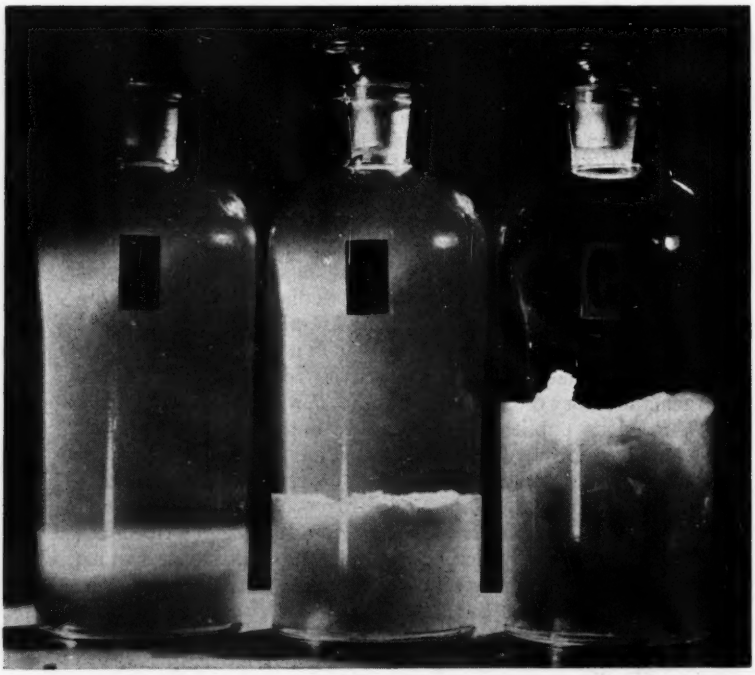


FIGURE 1. SEPARATION OF SOL AND GEL RUBBER BY DIFFUSION

The writers' experience has been that petroleum ether is a more reliable medium than ethyl ether for effecting a separation of sol and gel rubber. With ethyl ether a disintegration and dispersion of the gel rubber sometimes occur. In several controlled experiments using two different brands of technical absolute ether, it was possible to show that with one of them the disintegration always occurred whereas with the other it did not. The cause of this disintegration would, therefore, appear to be some impurity which may be present in ethyl ether (*24*). The difference in the diffusion process is illustrated in Figure 1. Each liter bottle contained 15 grams of acetone-extracted pale crepe rubber. Bottle *A* was

filled with the ethyl ether which caused disintegration of the gel rubber. In bottle *B*, which was also filled with ethyl ether, the diffusion proceeded in the normal manner. Bottle *C* was filled with petroleum ether. The photograph was taken after the bottles had stood in the refrigerator for 2 months. The gel rubber in *C* retained more strength than in *B*, as is apparent from its greater resistance to settling. However, the sol rubber from *B* and *C*, redissolved in purified ethyl ether, gave solutions for which the intensity of the

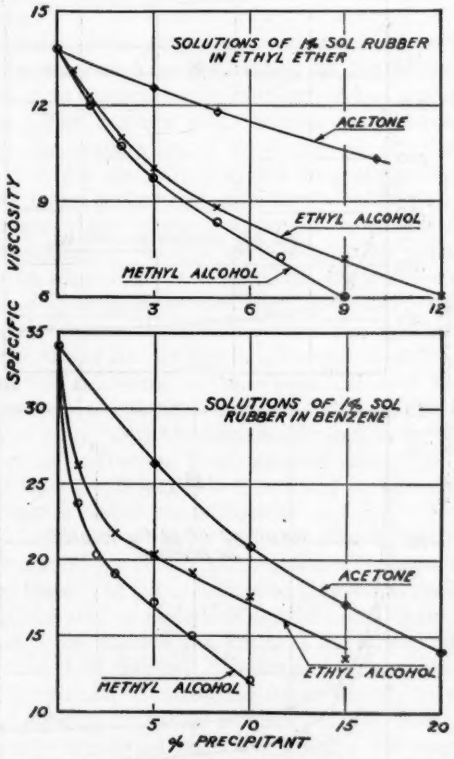


FIGURE 2. VISCOSITY CHANGES CAUSED BY ADDITION OF PRECIPITANTS

scattered light was practically identical. From this and similar experiments, as well as from the other evidence available in the literature (*12*, *20*), the writers believe that it is possible to effect a much better separation of the sol and gel rubber by the process of diffusion than is implied in the report of Midgley and Henne's experiment where some abnormal disintegration or oxidation of the rubber seems to have occurred.

Viscosity Effects

The addition of a precipitant, such as methyl alcohol, to a rubber solution, even in a much smaller amount than is required for precipitation, causes such a marked de-

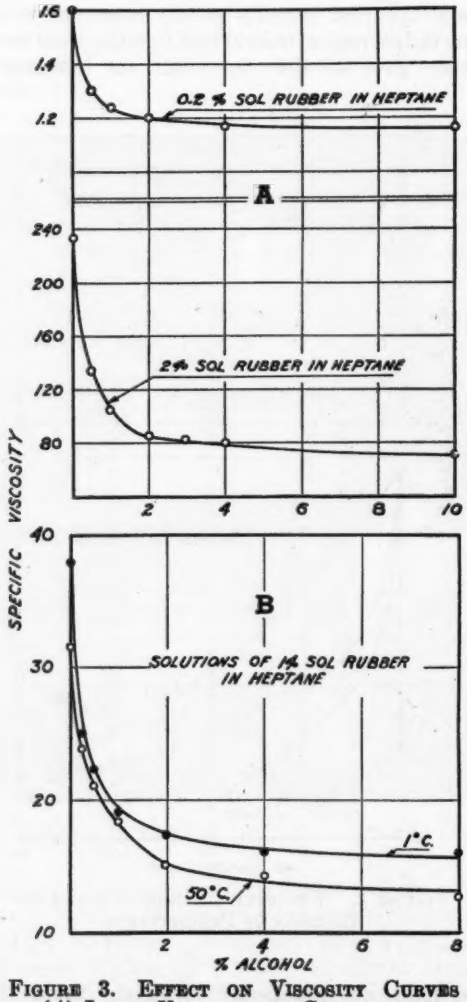


FIGURE 3. EFFECT ON VISCOSITY CURVES OF (*A*) LARGE VARIATION IN CONCENTRATION AND (*B*) TEMPERATURE

crease in the viscosity that a profound change in the colloidal structure may readily be suspected. Figure 2 gives typical curves illustrating how the viscosity of a rubber solution is altered by the addition of a precipitant. For the

curves of Figures 2 and 3, in contrast to most of those in the literature, the rubber concentration was kept constant as precipitant was added. This was done by the addition of an appropriate volume of more concentrated solution. The concentration of the precipitant, plotted as abscissa, is the volume of precipitant present divided by the volume of the solution after the precipitant is added, multiplied by 100. The viscosities were measured at 30° C. The solutions of Figures 2 and 3 were exposed to air during the measurements, but a control solution showed a negligible change in viscosity during the period of time taken for the measurements.

The effects of the precipitants upon the viscosity have been generally attributed to desolvation of the rubber, usually thought of as existing in the solutions in the form of swollen micelles. The authors wish to bring a different point of view to the explanation of these curves. In the previous work (*8*) it was deduced from the light scattering measurements that the rubber molecules formed clusters in solution, the size and shape of which depended upon the solvent and the concentration. One of the fundamental differences between such clusters and a colloidal micelle is that each cluster represents an equilibrium condition under the acting molecular forces, whereas the colloidal micelle is a discrete entity which maintains its identity in different solvents and in the solid rubber. A more accurate description of the clusters would probably represent them as having a statistical existence—i. e., as being continuously broken up by the thermal agitation and reforming to an average size. The decreased thermal agitation would help to account for the larger size of the clusters at higher concentrations.

The viscosity of a rubber solution depends not only upon the size and shape of the clusters but also upon the forces between them. It is inconceivable that the molecular forces between the rubber molecules should cause them to gather into such loose clusters and yet that the forces between the clusters could be ignored. Evidence for this dependence of the viscosity upon the molecular forces was given by showing that the dielectric molecular polarization of a series of solvents was closely correlated with the specific viscosities of the rubber solutions. The dielectric molecular polarization in itself cannot account for all the viscosity phenomena. For this purpose, a more exact mathematical representation of the molecular forces involved would be required. As for solvation, there is no logical reason for assuming that it exists to any greater or lesser degree for long molecules than for short ones, so that its role in the viscosity phenomena for rubber solutions is, in most cases, probably of minor importance.

The addition of methyl or ethyl alcohol to a rubber solution, as shown in Figure 2, causes an abrupt decrease in the viscosity at first. The dielectric molecular polariza-

tion of the alcohols is high compared to that of benzene—52.1 for ethyl alcohol, 36.8 for methyl alcohol, and 26.3 for benzene. A viscosity decrease is therefore expected. For ethyl ether the dielectric molecular polarization is 54.5, so that the effects of the alcohols on the viscosity of this solvent are not so obvious. However, it is impossible to calculate the dielectric molecular polarization of such a mixture in an additive way. Thus, it has been shown (*10*) that the dielectric molecular polarization for an ethyl ether–ethyl alcohol mixture has a maximum value greater than that of either component at about 30 per cent alcohol. It is perhaps

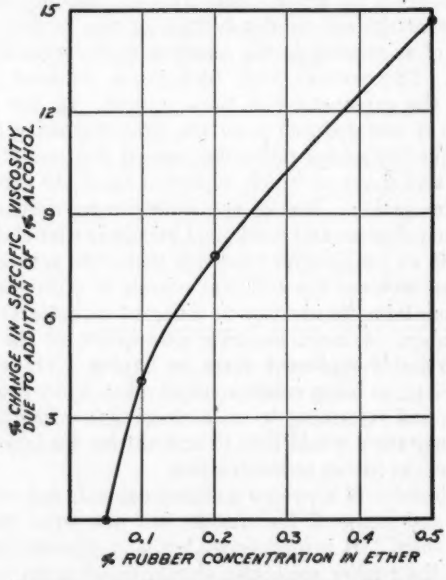


FIGURE 4. RELATION BETWEEN RUBBER CONCENTRATION AND REDUCTION OF VISCOSITY

with such a maximum that the abrupt change in slope of the viscosity curves upon further addition of precipitant is connected.

For a given solvent and precipitant, the position of the break in the viscosity curve is very insensitive to the rubber concentration, as shown in Figure 3*A*, and also to the rubber plasticity (*4*). This is evidence that the same forces are primarily responsible for the viscosity of these rubber concentrations.

The extent of the drop in viscosity at the "break" depends upon both the rubber concentration and the plasticity of the rubber. This dependence upon concentration is apparent in Figure 3*A* and also in Figure 4. Figure 4 shows the per

cent change in specific viscosity caused by the addition of one per cent of ethyl alcohol to rubber solutions of various concentrations in ethyl ether. The viscosities were measured in the sealed viscometer so that the solutions were not exposed to air at any time. The alcohol was contained in a sealed evacuated tube which was broken in the viscometer. The solvation would certainly be expected to be greater at the lower rubber concentrations so that these results cannot be reconciled with any interpretation based on desolvation as the cause for the decrease in viscosity.

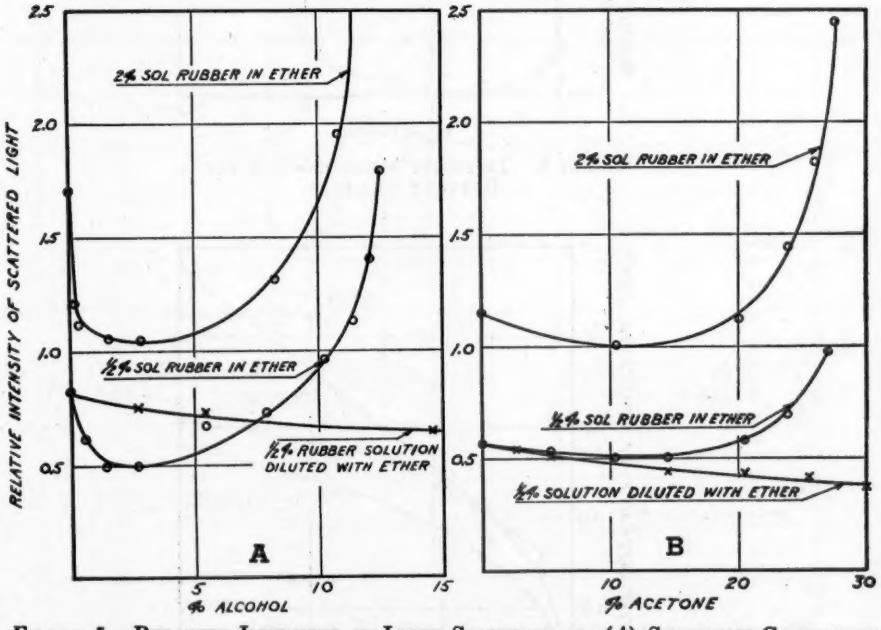


FIGURE 5. RELATIVE INTENSITY OF LIGHT SCATTERED BY (*A*) SOLUTIONS CONTAINING ALCOHOL AND (*B*) SOLUTIONS CONTAINING ACETONE

Figure 3*B* shows that the effect of the temperature on the specific viscosity is rather small even when a precipitant is present. This results from the fact that the absolute viscosities of the solution and the solvent have the same functional relation with the temperature; therefore their ratio, from which the specific viscosity is calculated, is not so much affected. This again is evidence for the existence of a molecular structure in the rubber solution similar to that now identified with the liquid state. For some rubber solutions the specific viscosity actually shows a small increase with increase in temperature. The changes in specific viscosity of the rubber solutions due to temperature do not appear to be ex-

plicable on the basis of changes in the dielectric molecular polarization of the solvents.

A comprehensive and precise investigation of the viscosity changes due to precipitants in terms of all the variables in-

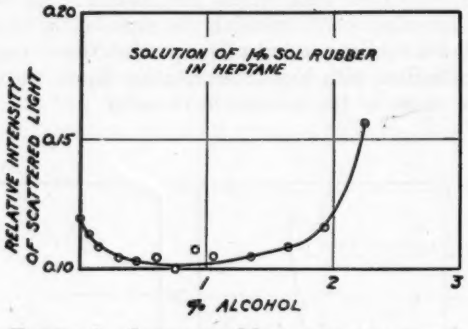


FIGURE 6. INTENSITY MEASUREMENTS FOR A HEPTANE SOLUTION

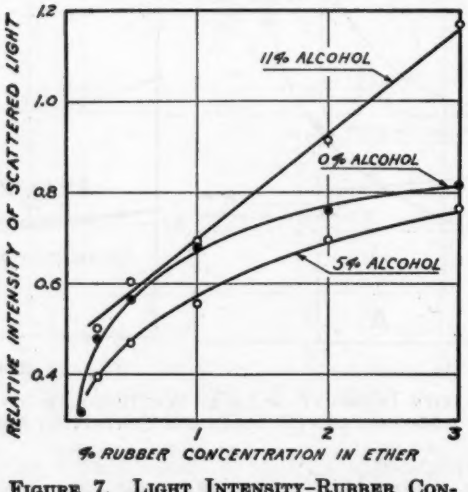


FIGURE 7. LIGHT INTENSITY–RUBBER CONCENTRATION CURVES FOR SOLUTIONS CONTAINING ALCOHOL

volved, especially in relation to the dielectric constants and molecular polarizations of the solvent and precipitant mixture, should be of considerable interest for the study of the colloidal structure of rubber in solution. This work, however, was limited to the study of the colloidal changes occurring in a few typical cases; measurements of the intensity and depolarization of the transversely scattered light were largely utilized.

Intensity of Scattered Light

The measurements illustrated in the curves were carried out on solutions which were exposed to air for the addition of the precipitants. However, enough measurements were made in sealed evacuated cells, where the precipitant was added by breaking a sealed tube, to ensure that the results here given were not significantly affected by the exposure. The use of ethyl ether and heptane solutions, for which the intensity of the scattered light is fairly high, rendered dust contamination less important than it would have been for solvents of higher refractive index. The solvents and precipitants used had approximately the same refractive indices.

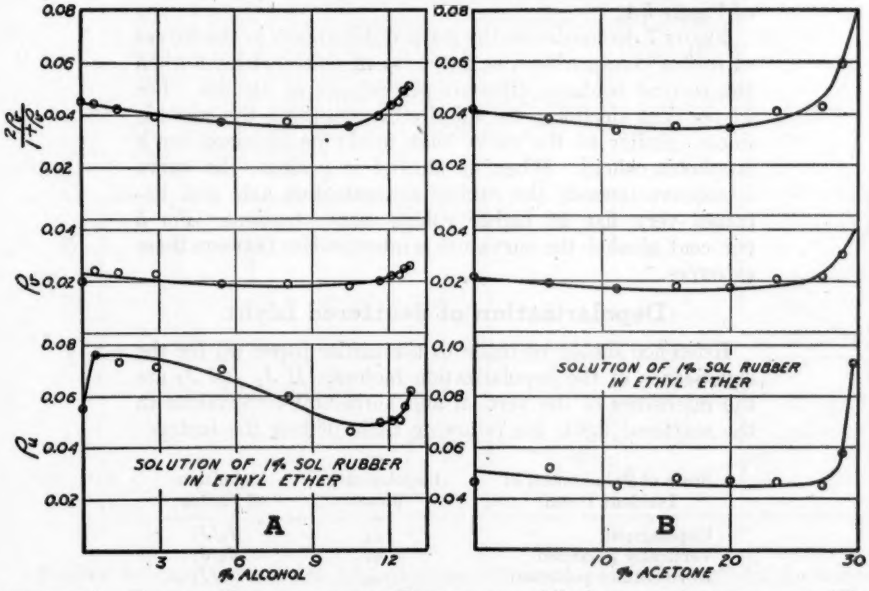


FIGURE 8. PLOT OF DEPOLARIZATION FACTORS FOR (*A*) ALCOHOL ADDITION AND (*B*) ACETONE ADDITION

Figure 5*A* shows the effect of alcohol on the relative intensity of the scattered light for ethyl ether solutions of sol rubber at several concentrations. For comparison, the straight line in the figure shows the change in intensity for the 0.5 per cent rubber solution due to dilution with the corresponding volume of solvent. The addition of the first trace of alcohol causes a sharp drop in the intensity. At a concentration somewhat less than that of the break in the viscosity curve, the intensity curve becomes flat; then at higher concentrations of alcohol it rises rapidly, a change not shown by the viscosity curves.

Figure 5*B* gives the changes in the relative intensity of the scattered light caused by the addition of acetone to

ethyl ether solutions of sol rubber. In contrast to the curves of Figure 5*A*, the curves for acetone addition do not have an abrupt initial drop. The slight dip in the curves can be explained as being due to the dilution. This is apparent from the straight line representing the decrease in intensity for the one per cent solution caused by dilution with solvent. Furthermore, when the rubber concentration was kept constant by addition of the required volume of a more concentrated solution, the dip was absent and the curves showed a very gradual rise from the start.

Figure 6 shows that the addition of alcohol to a heptane solution causes an initial drop in the intensity of the scattered light which is followed by a steep rise, similar to the curves of Figure 5*A*.

Figure 7 demonstrates the marked differences in the curves of rubber concentration *vs.* intensity of scattered light when the solvent contains different percentages of alcohol. For 11 per cent alcohol in the ethyl ether solutions, the curve is linear, similar to the curve that would be obtained for a lyophobic colloid. When no alcohol is present, the curve is concave towards the rubber concentration axis and becomes very flat at higher rubber concentrations. For 5 per cent alcohol the curvature is intermediate between these extremes.

Depolarization of Scattered Light

Reference should be made to the earlier paper (*8*) for the significance of the depolarization factors. If J_1 and J_2 are the intensities of the vertical and horizontal components in the scattered light, the following table defines the factors:

State of Polarization of Incident Beam	Depolarization Factor	Definition of Factor
Unpolarized	ρ_u	J_2/J_1
Vertically polarized	ρ_v	J_2/J_1
Horizontally polarized	ρ_h	J_1/J_2

The interpretation of the depolarization measurements here given is in accordance with the theory developed by Krishnan. Mueller (*17*) recently suggested an alternative explanation which can be considered only tentative. Gans (*7*) criticized one of Krishnan's formulas. The writers' experimental results favor the formula of Krishnan rather than that of Gans. Gans' formula gives consistently low values of ρ_u as calculated from ρ_h and ρ_v, which is not in accord with his idea that the failure of his formula to agree with experimental results is due to experimental errors in ρ_v.

The curves of Figure 8*A* illustrate the effect of alcohol addition on ρ_u, ρ_v, and the anisotropy factor, $2\rho_v/(1 + \rho_v)$, for a one per cent solution by volume of sol rubber in ethyl ether.

Figure 8*B* gives the same curves for acetone addition. In

Figure 9*A* are plotted the factors ρ_λ and $\Delta\rho_u = \rho_u - \frac{2\rho_v}{1+\rho_v}$, for alcohol addition, and in 9*B*, the same factors for acetone addition. The form of the curves was verified for concentrations of rubber from 3 to 0.5 per cent. Figure 10 shows the results of light scattering measurements for the addition of acetone to a 1 per cent solution of sol rubber in heptane.

Discussion of Results

In attempting to correlate the viscosity and light scattering results, it is necessary to keep in mind that the light scattering phenomena are due to the geometrical distribution and orientation of the rubber molecules in the solution. The viscosity, on the other hand, depends in a sense upon the stability of the structure or, more precisely, on the energy required to displace a unit of the structure (*19*). In the earlier paper (*8*) it was shown that the colloidal units responsible for the light scattering are probably anisotropic clusters or groups of rubber molecules which are large compared to the wave length of light.

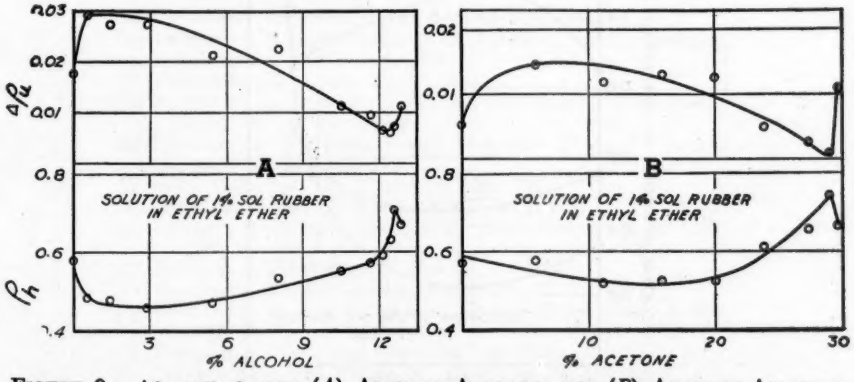


FIGURE 9. $\Delta\rho_\mu$ AND ρ_λ FOR (*A*) ALCOHOL ADDITION AND (*B*) ACETONE ADDITION

Since an increase in $\Delta\rho_u$ and a decrease in ρ_λ correspond to an increase in size of the scattering unit, the curves of Figures 9 and 10 are consistent in indicating an increase in size of the clusters as the first effect of the addition of precipitant. The anisotropy factor, $2\rho_v/(1+\rho_v)$ (Figure 8) is practically constant until the precipitation point is approached, when it rises rapidly. The initial increase in size of the clusters is consistent with the initial decrease in scattered light intensity observed in Figures 5*A* and 6. This decrease in intensity was not observed for acetone addition, however. Corresponding to the increase in the size of the light scattering units, there occurs a decrease in the specific viscosity. These facts may be qualitatively explained by considering that the first addition of precipitant influences the molecular forces in such a way that neighboring clusters

unite into larger units. This has the effect of diminishing the structure throughout the solution and causes the viscosity to fall. The structure of a rubber solution is thus represented as having a twofold character. There is structure in the colloidal units or molecular clusters, and there are structural "interlocking" relations of these units throughout the solution. As the precipitant is added, the structure in the colloidal unit approaches that of solid rubber, and the structure in the solution is progressively diminished until eventually precipitation occurs and the structure completely vanishes.

After the initial growth in size of the clusters, the light scattering measurements show further colloidal changes as

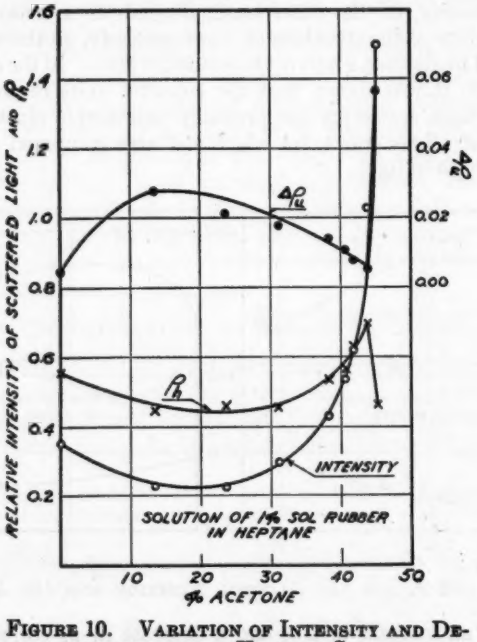


FIGURE 10. VARIATION OF INTENSITY AND DEPOLARIZATION OF A HEPTANE SOLUTION

precipitant is added. For alcohol addition to the ethyl ether solutions (Figure 5*A*) after the concentration of alcohol becomes approximately 3 per cent, the intensity curve rises continuously until precipitation occurs. This indicates that a breaking down of the scattering units occurs. This decrease in size is again verified by the changes in ρ_h and $\Delta\rho_u$ (Figures 9 and 10). ρ_h reaches its highest value near the precipitation point. The value at this point is higher than in the original solutions. The corresponding physical picture may be that the large clusters become unstable at higher concentrations of precipitant and break up to form a number of comparatively compact clusters with reduced solvation. This view is supported by the increase in the anisotropy factor.

When precipitation actually begins, the ends of the curves of Figure 9 indicate the growth in particle size which results in settling out of the rubber. The light scattering measurements at this point are sensitive to the temperature.

From the results and the discussion, it is apparent that the colloidal changes which take place upon the addition of precipitants to rubber solutions may advantageously be considered from the same standpoint as other fundamental problems dealing with the molecular forces and structure in liquids and solutions. Furthermore, the description of the solutions which has been offered tends toward a reconciliation between the extreme views of the exponents of the molecular and the micellar colloids. At higher rubber concentrations, the molecular clusters are so large and stable that the solutions have a micellar character; at very low concentrations, these clusters are so small and so subjected to thermal agitation that the colloidal phenomena approximate those which would be predicted as a result of the presence of individual threadlike macromolecules.

Literature Cited

(1) Caspari, W. A., *J. Soc. Chem. Ind.*, 32, 1041 (1913).
(2) Dawson, T. R., and Porritt, B. D., "Rubber," p. 67, Croydon, Rubber Research Assoc., 1935.
(3) Debye, P., *Chem. Rev.*, 19, 171 (1936).
(4) Fabritsiev, B. V., Buiko, G. N., and Pakhomova, E. A., *Rubber Chem. Tech.*, 9, 428 (1936).
(5) Faraday Soc., "Structure and Molecular Forces," London, Gurney and Jackson, 1936.
(6) Ford, T. F., *Ind. Eng. Chem.*, 28, 915 (1936).
(7) Gans, R., *Physik. Z.*, 38, 625 (1937).
(8) Gehman, S. D., and Field, J. E., *Ind. Eng. Chem.*, 29, 793 (1937).
(9) Herzfeld, K. F., *J. Applied Phys.*, 8, 319 (1937).
(10) Kanamaru, K., and Ueno, S., *Kolloid-Z.*, 79, 77 (1937).
(11) Kawamura, J., and Tanaka, K., *Rubber Chem. Tech.*, 5, 626 (1932).
(12) Kemp, A. R., *Ind. Eng. Chem.*, 30, 154 (1938).
(13) LeBlanc, Max, and Kröger, M., *Kolloid-Z.*, 33, 168 (1923).
(14) Lens, J., *Rubber Chem. Tech.*, 6, 265 (1933).
(15) Messenger, T. H., and Porritt, B. D., *J. Research Assoc. Brit. Rubber Mfrs.*, 1, 7 (1932).
(16) Midgley, T., and Henne, A. L., *J. Am. Chem. Soc.*, 59, 706 (1937).
(17) Mueller, H., *Phys. Rev.*, 52, 223 (1937).
(18) Schuls, G. V., *Z. physik. Chem.*, 179A, 321 (1937).
(19) Smallwood, H., *J. Applied Phys.*, 8, 505 (1937).
(20) Smith, W. H., and Saylor, C. P., *J. Research Natl. Bur. Standards*, 13, 453 (1934).
(21) Staudinger, H., and Heuer, W., *Z. physik. Chem.*, 171A, 129 (1934).
(22) Staudinger, H., and Mojen, J. P., *Kautschuk*, 12, 159 (1936); *Rubber Chem. Tech.*, 9, 579 (1936).
(23) Whitby, G. S., *Colloid Symposium Monograph*, 4, 203 (1926).
(24) Whitby, G. S., *Trans. Inst. Rubber Ind.*, 6, 40 (1930).
(25) Whitby, G. S., and Jane, R. S., *Colloid Symposium Monograph*, 2, 16 (1924).
(26) Whitby, G. S., McNally, J. G., and Gallay, W., *Ibid.*, 6, 225 (1928).

Translated for Rubber Chemistry and Technology from the Recueil des Communications du Congres International du Caoutchouc, pages 91–93, Paris, 1937.]

Observations on the Viscosity of Rubber Solutions

Eugene Guth*

A simple comparison is sufficient to show the great difference between a latex and a solution of rubber of the same concentration. The viscosity of rubber solutions is as a matter of fact very much greater. Furthermore, the viscosities of solutions of artificial rubber are still greater than those of solutions of crepe rubber.

This general difference in viscosity may be ascribed to a difference in shape of latex particles and that of particles of natural and artificial rubber in solutions. Latex particles are spherical, whereas the particles in solutions of natural and of artificial rubber appear to be long filaments.

Twenty years ago, Einstein in a fundamental work treated mathematically the problem of viscosity of suspensions of spherical particles. He found that the viscosity of a suspension of spherical particles in low concentration can be expressed by the following equation:

$$\eta = \eta_0 \left(1 + 2.5 \frac{V}{v}\right) \tag{1}$$

where η is the viscosity of the system and η_0 is the viscosity of the solvent.

The relative increase in viscosity, which may be called the "specific viscosity" in accordance with the terminology of Staudinger, is represented thus:

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

$$= 2.5\,c, \text{ where } c = \frac{v}{V} \tag{1a}$$

In this case certain assumptions have been made, *e. g.*, spherical particles of sufficiently great dimensions compared with the molecules of the solvent, negligible van der Waals forces, very dilute solutions, etc. The relation is independent of the state of dispersion in the total volume of a solution, but is directly proportional to the total volume of the dissolved particles.

An investigation of the limits within which the theory of Einstein is valid has been made by Guth and his collaborators in a series of papers,[1] which deal at the same time with the extension of Einstein's theory. Guth and Simha, and also Guth and Gold, deduced a formula which is applicable to solutions up to 6-per cent concentration if account is taken of the hydrodynamic interactions between the suspended particles:

$$\eta_{sp} = 2.5\,c + 14.1\,c^2 + \ldots\ldots \tag{2}$$

This formula was verified experimentally by suspending glass spheres in a proper medium.

With these formulas it is possible to calculate the viscosity of a suspension, *e. g.*, latex, when the total volume of the dissolved substances, the viscosity of the serum, and the total volume of the suspension are known, *i. e.*, the viscosity of latex of a

* Present address: Department of Physics, University of Notre Dame, Notre Dame, Indiana.

concentration (by volume) of v/V. Conversely, it is possible to calculate from the viscosity of a latex, as measured experimentally, the total volume of the particles in suspension.

The total volume of the latex particles can be obtained by determining their volume in the dry state. If, when calculated in this way, the relative viscosities of the latex agree with the measured values, it is evidence that there is no solvation and particularly no hydration of the latex particles in the serum. If, on the other hand, there are differences, it may be assumed that solvation has taken place, and in this case the solvation can be determined quantitatively by the difference between the volume measured in the dry state and the volume calculated by the Einstein formula or by formula (2) in the case of higher concentrations. As will be shown later in this article, there is appreciable solvation of the particles in crude latex and also of those in latex which has been purified several times.

In the next place, it can be shown that latices of the same concentration by volume but of differing degrees of purity have the same viscosities only at very low concentrations. To explain this phenomenon, it must be recalled that latex particles are surrounded by an electrokinetic layer of electrons in kinetic equilibrium.

Cataphoretic currents are set up by the relative movement between the liquid and solid interfaces arising from deformations of the diffused double layer. These currents and the electric potentials (cataphoretic potentials) created in this way lead, according to Thomson, Hardy, and Gouy, to a diminution in the relative mobility which the particles originally possess. The increase in viscosity caused by this phenomenon has been calculated in a quantitative way by Smoluchovski, but only the final result of his work has been published, since his premature death prevented him from including proofs of his conclusions. A more recent calculation by Krasny-Ergen, following the same general scheme, led to the same result, as that obtained by Smoluchovski, except for a factor of 3/2;

$$\eta_{rel} = \eta_0 \left\{ 1 + 2.5\,c \left[1 + \frac{3}{2} \cdot \frac{1}{\sigma \eta_0 a^2} \left(\frac{D\,\zeta}{2\pi} \right)^2 \right] \right\} \qquad (3)$$

where ζ is the potential of the diffuse double layer, σ the conductivity, D the electric constant of the serum, and a the radius of the latex particles. Formula (3) holds true if the product : σa^2 is of the order of magnitude of 4×10^{-3} and if, in addition, the conductivity σ of the serum is not too large and the radius of the latex particles is of the order of magnitude of 10^{-5} to 10^{-6} cm.

In any case at least, formula (3) makes it possible to explain differences in the viscosities of latices of the same volume concentration but of differing degrees of purity. It is evident that ζ-potential of latices of different degrees of purity will likewise be different. To this difference must also be added a difference in the solvation of latices of different degrees of purity, and this produces a double effect according to formula (3), *i. e.*, on the one hand, the radius of the latex particles changes and, on the other hand, the volume of the dispersed phase does likewise.

Particles in the form of rods behave differently, for then the ratio: $c = v/V$, etc., must each time be multiplied by a power of the axial ratio of the ellipsoid of rotation. A rod-shaped particle can be considered, as is well known, as the limiting case of an ellipsoid of rotation. This factor varies according to whether the particles are of large dimensions, in which case the Brownian movement of the axes can be ignored, or whether the particles are of small enough dimensions so that this movement is an essential factor.

In the first case the following formula, derived by Jeffery, Resp, and Guth,[2] is applicable:

$$\eta_{sp} = \gamma c + \mu c^2$$

$$\gamma_{min} \sim 2; \quad \gamma_{max} \sim \frac{l/d}{2(\ln 2l/d - {}^3/_2)} + 2 \tag{4}$$

Guth and Gold have likewise calculated μ in an exact manner for a deformation flow, and in an approximate way for a Couette flow.

For cases where the Brownian movement of the axes of the particles predominates, the following formula of Guth[3] is valid:

$$\eta_{sp} = \gamma c + \mu c^2$$

$$\gamma = \frac{(l/d)^2}{8(\ln 2l/d - {}^3/_2)} \sim 2.5 + \frac{1}{16}(l/d)^2 \tag{5}$$

The two expressions, derived initially on a hydrodynamic basis,[8] have recently been verified experimentally by Eirich and his collaborators,[4] who have shown that, for particles of sufficient length, *i. e.*, with no Brownian movement, the relation holds true as long as the length has any influence. The factor was found to be larger. Likewise measurements of suspensions of crystalline particles of definite form showed that, with increase in magnitude of the Brownian movement, formula (5) becomes progressively more nearly correct.

Although the two relations (4) and (5) are based on purely hydrodynamic concepts, *i. e.*, are to a certain extent idealized, they can at least to a certain extent be verified experimentally not only for model suspensions, but also for colloidal solutions. If, as believed by Staudinger, molecules with long chains are merely rigid rods which are subject to elastic vibrations when they are in solution, it would be expected that in a series of homologous polymers the specific viscosity would increase in proportion to the square of the length, and therefore in proportion to the square of the molecular weight. In reality researches during the last few years have demonstrated in a very certain manner that there is no well-defined law governing the relative viscosities of a series of homologous polymers as long as dilute solutions of short chains are concerned.[5] From a definite number of chain members (n = approximately 50 to a value corresponding to n = approximately 1000), the formula of Staudinger:

$$\eta_{sp} = K_m M c \tag{6}$$

is essentially correct.

The constant K_m depends on the temperature and on the solvent, but it varies (10–25 per cent) under definite conditions for a series of homologous polymers. Even if it cannot be credited with the status of a universal law, the relation of Staudinger contains certain elements of regularity which must be explained.

As has already been shown by Guth and Mark,[6] a statistical analysis of the interior of the molecules offers a possibility of explaining the problem, and at the same time gives a true quantitative picture of the facts, as has been demonstrated by the same authors and by Kuhn.[7] The internal mobility of the molecules is the cause of the transformation of chains into irregular structures resembling coils, and this results in an increase in the viscosity. To make any calculations, it would be necessary to obtain the "average shape" of the chain molecules. From its dimensions the increase in viscosity and its dependence on the concentration and on the molecular weight could be calculated by means of relations derived hydrodynamically.

This method offers, in the sense of a first approximation, a relation between specific viscosity and maximum length of chain, *i. e.*, molecular weight:

$$\eta_{sp} = K^m M^a c$$

According to the hypothesis used for calculating the "average shape" and for taking into account the van der Waals forces in the interior of the chains, the power α has values between 2/3 and 3/2. It is evident that a relation of a form analogous to that of Staudinger is obtained when "intramolecular" statistics, and also hydrodynamics, are applied to the case. If the hypothesis of rigid molecules is accepted, then the formula of Staudinger is invalid. The dependence of the Staudinger constant on the temperature and on the solvent, which has been found experimentally to be true, as well as the fact that formula (2) is valid only for chains above a certain length, are both arguments in favor of a statistical interpretation.

Some comparative measurements of the viscosities of solutions of crepe rubber and of Buna-S by means of a Hoepler viscometer were made. It was found possible to dissolve Buna-S in benzine after 40 min. of mastication on a cooled mill. This solution was used for the viscosity measurements. Crepe likewise was dissolved in benzine. The measurements are still not sufficiently extensive to make a comparison possible between these measurements and corresponding theoretical deductions. It is, however, obvious, even at this time, that solutions of Buna-S are much more viscous than those of crepe rubber of the same concentration; and it is possible to estimate the average length of the chains which are responsible for the viscosities of these solutions. This average length of chain is much greater in the case of Buna-S than in the case of crepe rubber.

References

[1] Guth, *Kolloid-Z.*, **74**, 147 (1936). Krasny-Ergen, *Ibid.*, **74**, 172 (1936). Guth, *Ibid.*, **74**, 15, 18 (1936). Guth and Simha, *Ibid.*, **74**, 266 (1936). Eirich, Margaretha and Bunzl, *Ibid.*, **74**, 266 (1936); **75**, 20 (1936). Simha, *Ibid.*, **76**, 16 (1936). Guth and Gold, unpublished work.

[2] Guth, *Kolloid-Z.*, **74**, 147 (1936).

[3] Guth and Gold, unpublished work.

[4] Eirich, Margaretha and Bunzl, *Ibid.*, **74**, 266 (1936).

[5] For very short chains, the hydrodynamic relations are no longer valid. For slightly longer chains, η_{sp} is represented by a complicated expression, which becomes simple only when $l/d > 1$. The statistical formulas for the "average shape" are also more complicated for a short than for a long chain.

[6] Guth and Mark, *Ergebn. exakt. Naturwissenschaften*, **12**, 115 (1933); *Monatsh.*, **65**, 93 (1934).

[7] Kuhn, *Kolloid-Z.*, **68**, 2 (1934). Kuhn's determination of the "average shape" for kinked chain molecules with free rotation at each joint is, however, unsound. Theory and experiment indicate a more elongated form of the average shape, as will be shown elsewhere.

[8] The limitations and ambiguities of the hydrodynamic theory of the viscosity of suspensions of rod-like particles will be pointed out in another paper.

[Reprinted from Industrial and Engineering Chemistry, Vol. 30, No. 9, pages 1036–1039, September, 1938.]

Chemistry of Soft Rubber Vulcanization*

Reversion and Nonreversion in Low-Sulfur Compounds

B. S. Garvey, Jr., and D. B. Forman

The B. F. Goodrich Company, Akron, Ohio

ACCUMULATION of evidence in recent years has led to a wide acceptance of the view that, chemically, vulcanization is the establishment of cross bonds between the fiber molecules of unvulcanized rubber. The usual concept is that of a chemical cross bond typified by the sulfur bridge (*4*). It was recently proposed (*2*) that "mechanical cross bonds" might be formed by the interlocking of the molecules as they become kinked as a result of *cis-trans* isomerization at some of the double bonds. It was also suggested that free rotation around single bonds might unkink the molecules. This straightening of the molecules would result in reversion of the vulcanized structure.

This theory suggested that a study of reversion would be of value. For this purpose low-sulfur compounds are most suitable because the number of chemically stable sulfur bridges is small. Consideration of the experiments reported here suggests the interesting possibility that in vulcanized compounds there exists a sort of dynamic equilibrium between the formation of cross bonds and their destruction, which results in the maintenance of an adequate number of cross bonds although the individual cross bonds are not permanent.

The general methods of mixing, curing, and testing were previously described (*3*). Since PBA and Altax gave the most clear-cut distinctions between reverting and nonreverting types of acceleration, the complete data are given for these two accelerators. Similar tests were made with the other accelerators, but only the conclusions from them are reported here.

Reversion Tests

The base recipe used was:

First latex crepe	100.0
Zinc oxide (lead-free)	3.0
Sulfur	0.5
Accelerator	2.5

* Five articles in this series have appeared in *Industrial and Engineering Chemistry* [25, 1042, 1292 (1933); 26, 434, 437 (1934); 29, 208 (1937)].

The stocks were cured from 5 to 480 minutes at 142° C. (288° F.). Table I gives test data for the compounds accelerated with Altax and PBA.

The numbers under "Behavior on Mill" and "Solubility" refer to the classification previously described (*3*). The uncured stocks fall in class 0, according to these tests, which shows that they are unvulcanized. The PBA compound after 15 minutes is in class 5 by the first test and class 4 by the second, which indicates that it is well vulcanized. After 480 minutes it is in class 1 by both of these tests, which shows that it is only slightly vulcanized. The retentivity at 100° C. (212° F.), according to the Goodrich plastometer, drops from that of masticated rubber to that of vulcanized rubber and rises again to that of rubber which is only slightly vulcanized. The same is true of the thermoplasticity (P^2_{100}/P_{30}). The rise and fall of the tensile strength and modulus likewise indicate vulcanization followed by reversion. With the Altax compound, on the other hand, all of the data change from those for unvulcanized rubber to those for well-vulcanized rubber and stay there. Little or no reversion takes place.

TABLE I. DATA FOR COMPOUNDS ACCELERATED WITH ALTAX AND PBA

Cure at 142° C.	Behavior on Mill	Solubility	R_{100}	P^2_{100}/P_{30}	Tensile Strength At 600%	Tensile Strength Ultimate	Elongation	Free Sulfur[a]
Min.					*Kg. per sq. cm.*		%	%
				PBA as Accelerator				
0	0	0	79.4	459.8	..	..	..	..
5	4	3	15.4	1.8	21.1	118.1	925	..
10	5	4	11.0	0.9	24.6	116.0	900	..
15	5	4	24.1	4.1	24.6	140.6	920	..
20	..	..	..	..	..	..	..	0.07
30	4	4	10.9	0.8	18.3	109.7	940	0.01
60	4	4	13.0	1.1	14.8	113.9	1000	..
120	4	4	10.8	1.0	5.6	42.2	970	..
240	3	3	15.4	2.6	11.2	18.3	1200	..
360	2	2	17.0	4.3	7.0	14.1	1120	..
480	1	1	19.5	8.5	3.5	4.2	850	..
				Altax as Accelerator				
0	0	0	81.9	423.0	..	..	..	..
5	1	0	78.8	372.6	..	3.2	1015	..
10	1	1	54.6	145.3	..	4.9	1015	..
15	2	1	25.9	11.4	..	10.9	1000	..
20	..	..	..	..	..	..	..	0.15
30	5	4	9.0	0.8	24.3	99.5	840	0.09
60	5	4	6.7	1.2	45.0	164.5	785	0.01
120	5	4	6.6	0.4	42.2	150.5	800	..
240	5	4	5.7	0.5	35.2	163.1	835	..
360	5	4	5.4	0.3	29.9	148.7	820	..
480	5	4	5.8	0.5	29.1	151.1	850	..

[a] Method of Oldham, Baker, and Craytor (*5*).

Corresponding data for other commercial accelerators led to the following classification:

Reverting Type	Nonreverting Type
Hexa (hexamethylene tetramine)	Monex (tetramethylthiuram monosulfide)
D. P. G. (diphenylguanidine)	Safex (dinitrophenyl ester of dimethyldithiocarbamic acid)
PBA (polybutyraldehyde-aniline)	Captax (mercaptobenzothiazole)
Vulcone (acetaldehyde-aniline)	Altax (mercaptobenzothiazyl disulfide)
MPT (methylene *p*-toluidine)	Tuads (tetramethylthiuram disulfide)

Vulcanizing Action of Accelerators

To study the behavior of accelerators alone as vulcanizing agents, sulfur was omitted from the above recipe. The stocks were cured 15, 60, and 120 minutes at 142° C. Only Tuads was sufficiently effective as a vulcanizing agent to develop appreciable tensile strength. Plasticity data, however, show definitely that several accelerators have a distinct vulcanizing action in the absence of sulfur. The test data for the PBA and Altax compounds are given in Table II.

For the PBA compound, retentivity, softness, plasticity at 30° and 100° C. (86° and 212° F.), and thermoplasticity all show small increases. There is no evidence of vulcaniza-

TABLE II. VULCANIZING ACTION OF ACCELERATORS WITHOUT SULFUR

Cure at 142° C. *Min.*	R_{30}	S_{30}	P_{30}	R_{100}	S_{100}	P_{100}	$\frac{P_{100}}{P_{30}}$
			PBA as Accelerator				
None	34.3	15.0	5.16	79.0	52.0	41.3	330
15	37.8	16.7	6.30	83.2	58.2	48.3	370
60	42.5	18.1	7.8	86.6	62.0	53.6	369
120	39.0	16.5	6.4	85.2	62.6	53.2	442
			Altax as Accelerator				
None	36.1	11.6	4.22	67.2	40.8	27.3	177
15	34.3	13.5	4.60	57.6	39.1	22.5	110
60	31.6	14.1	4.62	53.5	36.5	19.5	82
120	26.8	12.2	3.26	33.5	25.2	8.4	22

tion. With the Altax compound, however, all of these values drop significantly and give definite evidence of a certain amount of vulcanization, although the compound does not become well cured.

These and similar data permit the following classification of the ten accelerators:

Vulcanizing Type		Nonvulcanizing Type	
Monex	Altax	Hexa	Vulcone
Safex	Tuads	D. P. G.	MPT
Captax		PBA	

Reclaiming and Recuring

Using the same base recipe as in the reversion tests, a number of tensile sheets containing each accelerator were cured in the optimum time. They were then reclaimed by milling on a hot refiner (about 100° C.) for 30 to 60 minutes. The reclaims were cured 15 and 60 minutes at 142° C., both with 0.5 per cent of sulfur (C-cure) and without additional sulfur (B-cure). The cured sheets from the reclaims were in all cases of poorer quality than the original stocks. Test data for the PBA and Altax compounds are given in Table III.

The plasticity data show that the PBA stock was well reclaimed and that it did not become vulcanized in the B-cure (without sulfur). In the C-cure (with 0.5 per cent sulfur), however, the compound again became definitely vulcanized, as shown by both plasticity and tensile data. The plasticity data show that the Altax compound, too, was well reclaimed.

TABLE III. EFFECT OF RECLAIMING AND RECURING ON ACCELERATED STOCKS

	Cure at 142° C. *Min.*	R_{30}	S_{30}	P_{30}	R_{100}	S_{100}	P_{100}	$\frac{Ph_{100}}{P_{30}}$	Tensile Strength *Kg./sq. cm.*	E %
PBA as Accelerator										
Reclaim	None	42.6	41.8	17.8	90.2	78.9	71.2	282	...	...
B-cure	15	39.4	49.0	18.2	80.0	75.0	67.1	247	...	...
B-cure	60	43.4	50.2	21.8	90.0	81.0	73.0	244	...	...
C-cure	15	7.2	8.2	0.6	7.6	8.5	0.6	0.6	105.5	890
C-cure	60	9.8	10.0	1.1	8.4	11.4	0.96	0.84	45.7	920
Altax as Accelerator										
Reclaim	None	13.0	16.2	2.1	49.3	46.0	22.6	243	...	...
B-cure	15	7.6	11.4	0.87	7.6	12.8	1.0	1.15	42.2	810
B-cure	60	6.7	10.9	0.74	6.6	11.0	0.73	0.72	63.3	850
C-cure	15	6.5	8.3	0.55	8.1	8.7	0.70	0.89	77.3	810
C-cure	60	4.0	9.0	0.36	8.1	9.3	0.76	1.6	84.4	830

In this case, however, the compound became vulcanized after both the B- and C-cures, as shown by plasticity and tensile data.

The data from similar experiments with all of the accelerators may be summarized as follows:

Accelerator	Initial A-Cure	Reclaim	B-Cure without sulfur	C-Cure with sulfur
Hexa	Fair	Good	Very slight	Slight
D. P. G.	Fair	Good	No cure	Poor
PBA	Good	Good	No cure	Good
Vulcone	Good	Good	No cure	Slight
MPT	Poor	Good	No cure	Poor
Monex	Good	Poor	Good	Good
Safex	Good	Good	Slight	Fair
Captax:				
10 min.	Good	Good	Good	Good
120 min.	Good	Good	No cure	Fair
Tuads	Good	Poor	Good	Good
Altax	Good	Good	Good	Good

Results

These accelerators fall definitely into two groups. Those in the first group show no vulcanizing action in the absence of sulfur, give a reverting stock with low sulfur, and after mill reclaiming require the addition of more sulfur to cure. Those in the second group show definite vulcanizing activity in the absence of sulfur, give a nonreverting stock with low sulfur, and after mill reclaiming will cure without the addition of more sulfur. The amino accelerators are all in the first group and those containing sulfur are in the second group.

Certain individual characteristics of some of the accelerators may also be mentioned.

Hexa is a very slow accelerator, and the slight C-cure is probably due to free sulfur left from the original cure.

Vulcone appears to be a typical reverting accelerator. The results of the C-cure indicate, in addition, that it is somewhat fugitive.

The poor reclaims obtained with Monex and Tuads indicate either that these two accelerators may liberate sulfur and thus give stocks with considerably greater amounts of combined sulfur than the other accelerators, or that they are sufficiently active as vulcanizing agents on a hot mill so that they can counterbalance the devulcanizing action of the milling.

Safex appears to have just enough curing action to prevent serious reversion but not enough to give a good B-cure. It may be somewhat fugitive.

Mercaptobenzothiazole seems to be a typical curing and nonreverting accelerator but the B- and C-cures after the 120-minute A-cure indicate that it is somewhat fugitive.

Theoretical Discussion

The concept of dynamic equilibrium in vulcanized rubber can best be illustrated for these experiments by considering geometric rearrangement (*cis-trans* isomerism) as the mechanism of vulcanization and free rotation at single bonds as the mechanism of reversion. The mobility of the groups within the rubber molecules is in agreement with the kinetic theories of rubber structure (*1*).

Geometric rearrangement is assumed to occur during vulcanization and to result in kinking of the fiber molecules of crude rubber which are considered to be comparatively straight. This kinking would result in greatly increased mechanical entanglement—that is, in the establishment of mechanical cross bonds. Free rotation at single bonds under the influence of thermal agitation would permit the kinked fibers to become again comparatively straight. Hence there would be fewer mechanical cross bonds, and the stock would revert.

In low-sulfur compounds it is probable that there are com-

paratively few of the stable, chemical cross bonds (sulfur bridges) and that most of the vulcanization is by mechanical cross bonds. It might be expected, then, that in long cures such compounds would revert until there remained only that part of the vulcanized structure due to the sulfur bridges. In case this is not true, it may be assumed that there is enough continued vulcanizing action to rekink the molecules as fast as the heat straightens them out by free rotation. By this equilibrium mechanism the vulcanized structure persists although the individual cross bonds may not.

With certain accelerators vulcanizing action occurs only when free sulfur is present. Low-sulfur compounds with these accelerators are well vulcanized after heating a short time but revert badly on continued cure. Other accelerators exert definite but limited curing action without free sulfur. With the latter accelerators in low-sulfur compounds, there is rapid curing action until all of the sulfur is combined, after which there is a slow continuation of cure by the accelerator alone which counterbalances the reverting action of thermal agitation. The accelerators exert just enough vulcanizing action to rekink the molecules as fast as the heat straightens them.

These two types are well illustrated by comparing the reverting compound accelerated by PBA with the nonreverting Altax compound. PBA does not vulcanize rubber in the absence of sulfur and does not maintain its curing action after the sulfur is all combined. On the other hand, Altax shows a slight but definite vulcanizing action in the absence of sulfur and maintains its curing action throughout long cures.

In terms of this theory the results in Table I may be interpreted as follows: While free sulfur is present during the first 15 to 20 minutes of the cure with PBA, rearrangement (vulcanization) takes place rapidly. After the sulfur is all combined, the rearrangement stops and the straightening of the molecules under the influence of thermal agitation becomes preponderant. As this action continues, the product reverts until after 8 hours the only part of the vulcanized structure remaining is that due to the small number of sulfur bridges. With Altax, after the initial lag period of 10 to 15 minutes, rearrangement is rapid while free sulfur is present, and the product becomes vulcanized. In this case the tendency of thermal agitation to straighten the molecules after the sulfur is all combined is counterbalanced by the vulcanizing action of the accelerator itself. As fast as a kink is lost in one place by free rotation around single bonds, another kink is set up by rearrangement at a double bond so that the number of mechanical cross bonds is fairly constant although the individual cross bonds are not permanent. There is very little reversion, and the product remains well vulcanized even after the 8-hour cure.

Literature Cited

(1) Busse, W. F., *J. Phys. Chem.*, **36**, 2862 (1932); Griffith, T. R., *Can. J. Research*, **10**, 486 (1934); Guth, E., and Mark, H., *Monatsh.*, **65**, 93 (1934); Houwink, R., *India Rubber J.*, **92**, 455 (1936); Karrer, E., *Phys. Rev.*, [2] **39**, 857 (1932); Meyer, K. H., von Susich, G., and Valko, E., *Kolloid-Z.*, **59**, 208 (1932).
(2) Garvey, B. S., *Ind. Eng. Chem.*, **29**, 208 (1937).
(3) Garvey, B. S., and White, W. D., *Ibid.*, **25**, 1042 (1933).
(4) Meyer, K. H., and Hohenemser, W., *Helv. Chim. Acta*, **18**, 1061 (1935).
(5) Oldham, E. W., Baker, L. M., and Craytor, M. W., *Ind. Eng. Chem.*, Anal. Ed., **8**, 41 (1936).

[Translated for Rubber Chemistry and Technology from Naturwissenschaften, Vol. 26, No. 1, pages 12–13, January 7, 1938.]

The Rubber-like Behavior of an Artificial Substance (Oppanol) when Irradiated with X-rays

R. Brill and F. Halle

THE OPPAU RESEARCH LABORATORY OF THE I. G. FARBENINDUSTRIE A.-G., LUDWIGSHAFEN A. RHEIM

As is known, natural rubber has the property of giving, when stretched, an x-ray fiber diagram, whereas in a normal state the same rubber is amorphous. Numerous other natural substances such as hair and tendon, and artificial substances such as polychloroprene, behave in the same way. However, this effect is not confined to

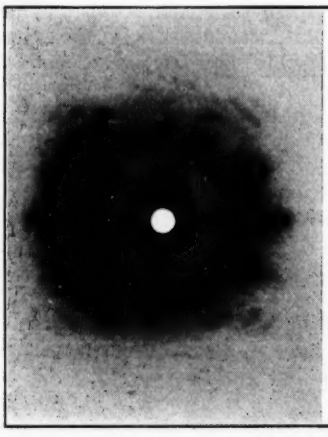


Figure 1—Roentgen Diagram of Stretched Rubber

This photograph and that of Fig. 2 were taken under identical conditions

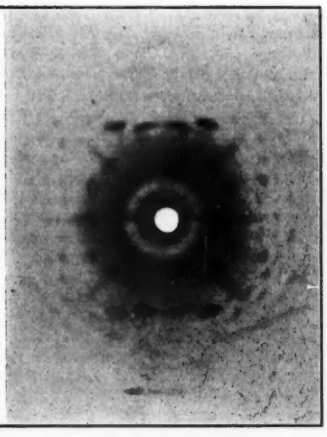


Figure 2—Roentgen Diagram of Stretched Oppanol

This photograph and that of Fig. 1 were taken under identical conditions

purely organic substances, and it is to be found, for example, in the case of so-called amorphous sulfur[1] and polyphosphornitryl chloride $(PNCl_2)_x$.[2] All these substances have the property in common with one another of exhibiting a rubber-like elasticity within a definite temperature range, and of being composed of long-chain molecules.

This rubber-like behavior is particularly striking in the case of the artificial substance Oppanol. Oppanol is a substance which superficially resembles rubber very closely. At room temperature it can be stretched reversibly to approximately 15 times its original length, under which conditions it becomes warm just as natural rubber does. When the tension is released, it cools again. In the stretched con-

dition it gives, as does natural rubber, an excellent x-ray fiber diagram, whereas in the normal state it is roentgenographically amorphous. The x-ray diagram of stretched Oppanol is essentially different from the x-ray diagrams of the natural and artificial substances mentioned above, as may be seen by a comparison of Figs. 1 and 2. All those substances, including natural rubber, show, when stretched, fiber diagrams which give, by calculation, relatively small identity periods in the direction of stretching, *e. g.*, natural rubber[3] 8.20 A. U., keratin[4] approximately 7.20 A. U., polychloroprene[5] 4.8 A. U., and polyvinyl alcohol[6] 2.57 A. U. In contrast to this, the x-ray diagram of stretched Oppanol gives a fiber period of 18.50 A. U. From the fact that Oppanol is elastic and at the same time shows a fiber diagram when stretched, it may reasonably be concluded that the molecules of Oppanol also are in the form of chains. However, the length of the fiber period points to the fact that the molecular structure is not that of a planar zig-zag chain but most probably, in view of the presence of side groups, has a spiral form. This would be analogous to the structure of polymethylene oxide and polyethylene oxide,[7] which show practically the same phase periods.

References

[1] Meyer, *Trans. Faraday Soc.*, **32**, 148 (1936).
[2] Meyer, Lotmar and Pankow, *Helvetica chim. acta*, **19**, 930 (1936).
[3] Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936).
[4] Astbury, *Chem. Weekbl.*, **33**, 778 (1936).
[5] Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).
[6] Halle and Hofmann, *Naturwissenschaften*, **23**, 770 (1935).
[7] Sauter, *Z. phys. Chem.*, **21B**, 161, 186 (1933).

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 14, No. 1, pages 2–5, January, 1938; No. 2, pages 26–29, February, 1938.]

Determination of the Resistance of Vulcanized Rubber to Tearing

D. J. van Wijk

GOVERNMENT RUBBER INSTITUTE, DELFT, HOLLAND

Introduction

By the resistance to tearing of a material is meant the resistance shown by the material, while under tension, to tearing completely apart after a split has been made in the surface by any means whatsoever.

Without question, the destruction of rubber articles can in many cases be traced to tearing. The initial tears can be regarded as the result of a splitting of the inelastic oxidized skin or of injury to the surface. Tears on the side walls of a tire, for example, can be attributed to the first cause; the wear on the tread is attributable to the second cause mentioned above.

Resistance to tearing should therefore be regarded as one of the most important properties of rubber. The numerous and widely different methods which have been proposed and used for determining resistance to tearing are proof of this.

A complete survey of the literature to 1932 was published by Lefcaditis and Cotton. These authors described about twelve different methods for determining resistance to tearing, proposed a modified form of the method of Heidensohn, and determined the tear-resistance of various mixtures by this method. Subsequently, Lefcaditis[2] studied this method further, and determined the effect of fillers and of mastication on resistance to tearing.

In a publication which appeared soon afterwards, Talalay[3] showed the limitations involved in comparisons of results obtained by the various methods, and also showed the difficulties encountered in testing carbon black mixtures because of knotting, whereby the tear changes direction laterally, resulting in great variations in the measurements.

Similar measurements were made by Kirchhof[4] on films of Jatex-shellac mixtures and on vulcanized rubber sheets with calender grain. He suggested that a distinction be made between resistance to separation (on tearing in the direction of stretching or of calendering) and resistance to tearing (in a direction perpendicular to that mentioned).

The notably lower values of the resistance to separation compared with those of resistance to tearing are attributable to structural differences. Kirchhof proposed a special method for determining the resistance to separation of calendered sheets of rubber.

Clarke[5] described briefly three different methods for the determination of resistance to tearing. These very interesting methods were developed particularly for tires, and they are less suitable for determining the tear-resistance of rubber products of various types. The statement of this author that resistance to tearing is a function of tensile strength does not agree with experiences of the present author.

Busse[6] studied the stresses which are set up in test-specimens under tension with notches of various depths, and advanced a theory to explain resistance to tearing of

an isotropic elastic material. Busse was of the opinion that the knotting and branching of the tears in carbon black mixtures are caused by a fibrous structure formed during stretching.

In a recent publication, Farberov[7] pointed out the importance of testing tear-resistance, but he offered no suggestion as to the method to be used for this determination.

In a publication entitled "The effect of dispersing agents in loaded mixtures," Behre[8] mentions a method whereby the resistance to tearing is determined with two semicircular halves of a Schopper disc. The disc is cut straight across by means of a die-cutter, and at the same time both halves are provided with a cross-cut 1 cm. deep.

As already mentioned by Talalay,[3] most of the methods suggested for determining tear-resistance are the same in that the test-specimens are cut on one side and the

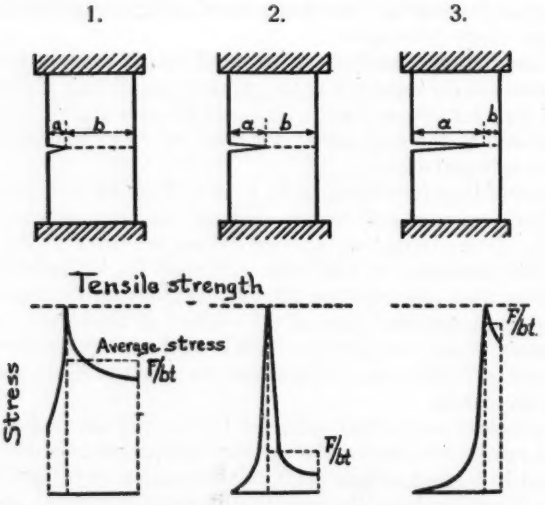


Figure 1—Diagram of W. F. Busse's Stress-Distribution in Cut Test-Specimens

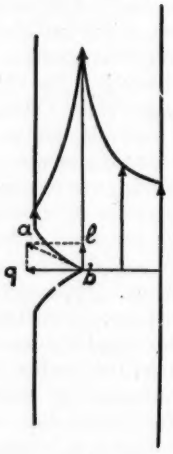


Figure 2—Stresses in a Cut Test-Specimen

two halves are pulled apart on a tensile testing machine. All these methods necessarily have the disadvantages mentioned above, especially in testing carbon black mixtures. As a result of tests which we have made by various methods, these disadvantages can be summarized as follows:

1. Changes in direction, knotting, and branching of the tears;
2. Great differences between the lowest and the highest values of the tear-resistance in an individual experiment (even 100 per cent of the mean value); and
3. Great differences in the values of repeated determinations (as great as 50 per cent of the mean value).

Object of the Present Experiments

The object of the present investigation was two-fold: (1) A practical object, *viz.*, the development of a method for measuring tear-resistance which either would not have the disadvantages described, or would possess them to only a slight degree,

and with which it would be possible to operate with standard test-specimens such as Schopper rings or small strips.

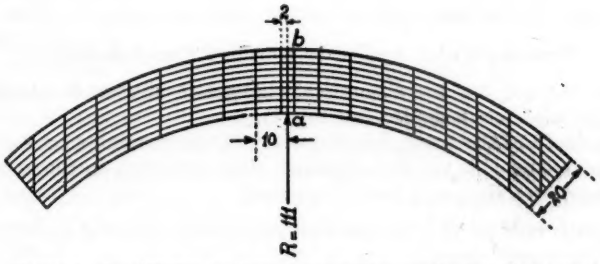


Figure 3—Bent Strips for Determining Stresses during Elongation

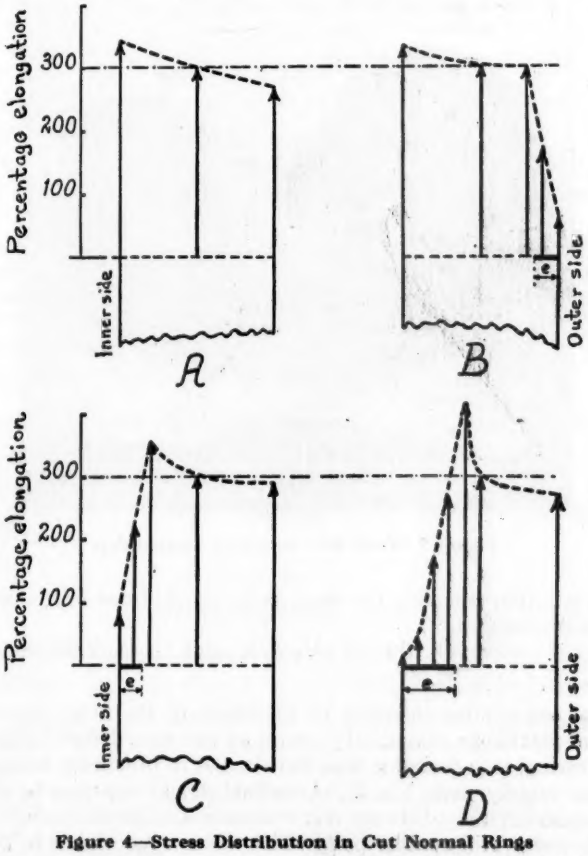


Figure 4—Stress Distribution in Cut Normal Rings

(2) A scientific object, *viz.*, an investigation to determine whether optimum resistance to tearing coincides with technical optimum tensile strength, *i. e.*, the strength which represents the best aging.

In the present work, we have confined ourselves chiefly to the first of these two objectives. However, before passing to a consideration of the practical method, it seems desirable to deal in some detail with the stresses which are set up in the experiments on tear-resistance.

Stresses Which Appear in Notched Test-Specimens

Busse[6] has worked out the theoretical changes in stresses in elongated strips having notches of different depths (see Fig. 1).

If a is the depth of the notch, b is the width of the remaining part of the strip, t is the thickness, and F is the force applied, then according to Busse the following three fundamental cases should be distinguished:

1. When a is very small. In this case the average stress at rupture, F/bt, approximates the tensile strength.

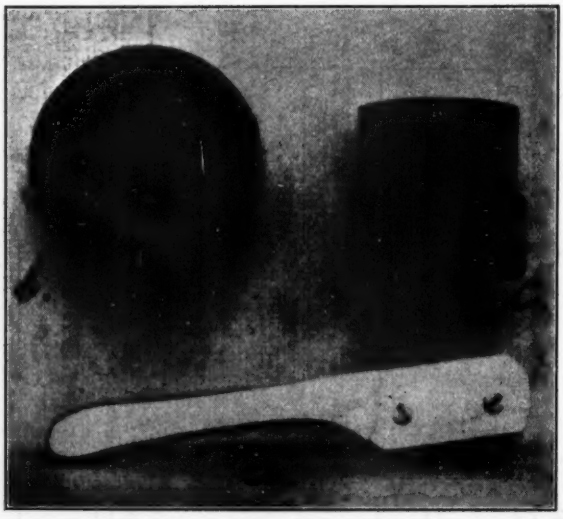


Figure 5—Knife and Accessory Implements

2. When a is approximately the same as b. In this case F/bt is much smaller than the tensile strength.
3. When b is very small. In this case F/bt again becomes the same as the tensile strength.

This makes evident the influence of the depth of the notch between definite minimum and maximum values. To assure an accurate determination of the resistance to tearing, it is desirable that the stresses in proximity to the end of the notch increase rapidly, as in Fig. 2. A method should therefore be chosen which gives the greatest difference between tear-resistance and tensile strength.

There is, however, still another point which was not mentioned in Busse's work, and which is of particular significance in a consideration of the process of tearing the rubber in two, *viz.*, the appearance of transverse stresses.

In Fig. 2 the stresses in a notched test-specimen under tension are represented schematically. In the bent part a-b of the cut, tangential stresses are present, and

these stresses can be resolved into longitudinal and transverse stresses (in Fig. 2 only the stresses at the end-point of the cut are shown).

The transverse stress q is the cause of the change in direction of the tear, and the deeper the cut the larger is this stress, so that for this reason too the maximum value of this depth is limited.

The diagram in Fig. 1 is concerned with straight strips, and hence is applicable to experiments with ordinary test-specimens.

Since it was of interest to obtain an idea of the stresses in standard ring specimens, bent strips 20 mm. wide and 5 mm. thick were prepared from a mixture of 100 parts of rubber, 5 parts of sulfur, 1 part of diphenylguanidine, and 20 parts of zinc oxide, vulcanized for 25 min. at 147° C. The dimensions (with the exception of the thickness) of the strip represented in Fig. 3 are five times as great as those of a standard ring.

The strips were marked with concentric lines and parallel lines, and cut at their centers to various depths. They were then elongated until the elongation of the neutral line was 300 per cent The elongation of the other concentric lines was determined, on sections originally 2 mm. long, on both sides of the cut transverse line *a-b*.

The results of the measurements, which are reproduced in Fig. 4, lead to the following conclusions:

1. With shallow cuts on the inner side (see Fig. 4C) the stress at the end of the cut was only a little greater than the stress on the inner side of an uncut ring (see Fig. 4A).
2. With cuts of twice the depth (see Fig. 4D) the tension increased considerably at the end of the cut.
3. With cuts on the outer side of the ring (see Fig. 4B) the stress at the top of the cut remained smaller than that on the inner side of the ring. Hence the ring breaks as soon as this latter stress reaches the value of the tensile strength. In this case therefore the cut has theoretically no effect.

Determination of the Tear-Resistance at Normal Velocity

It was necessary to determine experimentally the influence of the manner of making the cuts and the depths of the cuts on the results obtained. Accordingly, sheets 5 mm. thick were prepared from mixtures having the compositions given in the table below.

TABLE I

COMPOSITIONS OF THE MIXTURES

Ingredient	A	B	C
Rubber	100	100	100
Mineral rubber	..	8	..
Sulfur	5	3.5	5
Diphenylguanidine	1	1.25	1
Stearic acid	..	2	..
Machine oil	..	2	..
Zinc oxide	3	10	100
Carbon black (Micronex)	..	44.5	..
Whiting	..	...	50
Minutes of vulcanization at 147° C.	25	40	20

Standard ring specimens and test-strips[9] were died out from these vulcanized sheets.

The resistance to tearing was determined after having made notches in various ways and to various depths. The tensile strengths likewise were determined. The rate of travel of the lower grip of the dynamometer was 50 cm. per minute.

The cuts were made with a razor blade in a holder. The flat surfaces on each side of the razor blade were about 6 mm. wide. The distance that the blade projected from its clamps could be accurately adjusted by means of a microscopic scale. The blade in its holder is illustrated in Fig. 5.

The standard rings were in all cases notched at diametrically opposite locations; the test-strips were notched in the middle of the prismatic part. Wooden implements were used for notching the standard rings, and these are illustrated in Fig. 5 (b and c); b, for notching the upper and lower surfaces, c, for the outer side and inner side. The test-strips were notched by free hand.

The resistance to tearing is expressed in kg. per sq. cm. of the torn cross section.

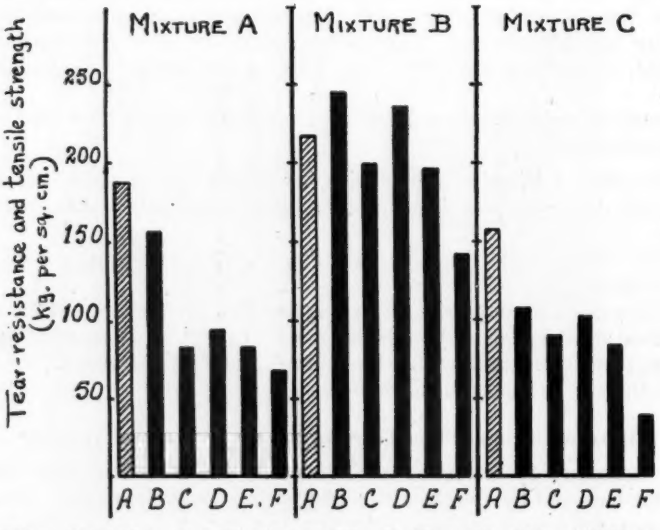


Figure 6—Resistance to Tearing and Tensile Strength of Normal Rings

A = Tensile strength
B = Tear-resistance—0.5 mm. incision outer side
C = Tear-resistance—0.5 mm. incision inner side
D = Tear-resistance—0.5 mm. incisions on the outer and inner sides
E = Tear-resistance—0.5 mm. incisions on all sides
F = Tear-resistance—1.0 mm. incisions on all sides

(*a*) *Influence of the Type of Cut.*—The test-specimens were notched 0.5 mm. deep as follows:

Rings: outer side; inner side; outer side and inner side; all sides.

Strips: left side; left side and top side; top side and lower side; all sides.

The results of the tests are summarized in Table II, and shown in diagrammatic form in Figs. 6 and 7.

(*b*) *Influence of the Depth of Cut.*—The influence of the depth of the notch was likewise determined for both standard rings and test-strips, which were notched to a depth of 1 mm. The results, which are included in Table II and shown diagrammatically in Figs. 6 and 7, lead to the following conclusions:

1. With shallow cuts on the outer side and on the inner and outer sides of stand-

ard rings of the carbon black mixture B, the tear-resistance was greater than the tensile strength. This phenomenon is in accord with stress diagram in Fig. 4. With this particular mixture B, a notch on the outer side meant only that the width of the ring was decreased, and consequently a higher tensile strength was obtained. In this case tear-resistance played no part.

2. Notches on all sides gave the greatest differences between the values for tear-resistance and tensile strength, and this was true of all three mixtures.

3. With notches 1 mm. deep, the differences in the values of tear-resistance and strength were considerably greater than with notches 0.5 mm. deep.

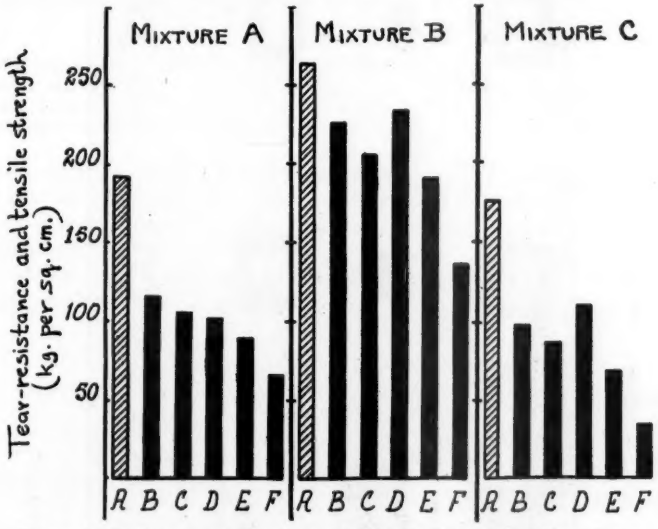


Figure 7—Resistance to Tearing and Tensile Strength of Test-Strips

A = Tensile strength
B = Tear-resistance—0.5 mm. incision on left side
C = Tear-resistance—0.5 mm. incisions on left and upper sides
D = Tear-resistance—0.5 mm. incisions on upper and lower sides
E = Tear-resistance—0.5 mm. incisions on all sides
F = Tear-resistance—1.0 mm. incisions on all sides

TABLE II

Type of Notch	A	B	C
Standard rings			
Tensile strength	188	217	157
Tear-resistance			
Outer side 0.5 mm.	157	245	108
Inner side 0.5 mm.	83	200	89
Outer and inner sides 0.5 mm.	94	235	102
All sides 0.5 mm.	83	197	83
All sides 1 mm.	68	142	38
Test-strips			
Tensile strength	192	264	175
Tear-resistance			
Left side 0.5 mm.	115	225	98
Left side and top side 0.5 mm.	106	206	86
Top side and lower side 0.5 mm.	102	234	110
All sides 0.5 mm.	90	192	67
All sides 1 mm.	66	136	33

With still deeper cuts the cross sections to be torn were so small that the results were less precise, and one is therefore justified in assuming that notches 1 mm. deep were correct.

It was noticed during the experiments that test-specimens from mixture B, with notches 1 mm. deep on all sides, tore apart around a definite stress with a clear tear. In these cases no knotting was observed.

In Fig. 8, a few cut surfaces of rings from mixtures A and of strips from mixture

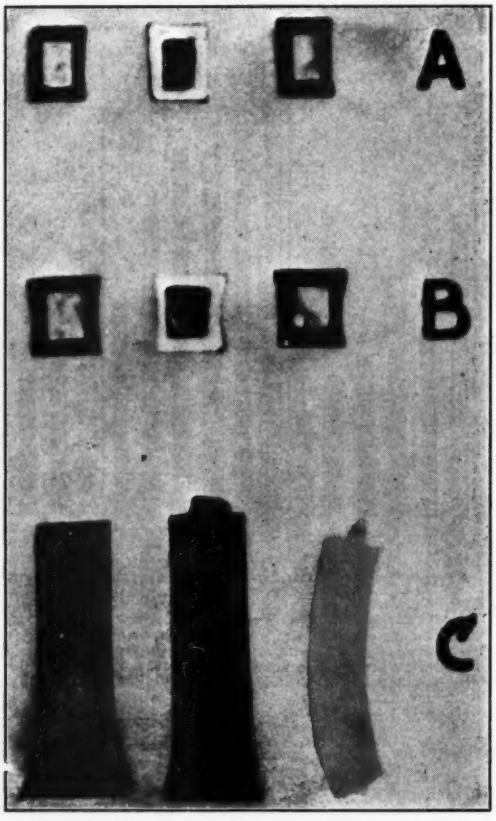


Figure 8—Cut Sections of Completely Torn Test-Specimens

B are shown. The cut parts of the white mixture are colored black; the cut parts of the black mixture are colored white. The samples shown in Fig. 8C did not tear apart on a flat surface; however, they did not give abnormal results.

(*c*) *Accuracy of the Cuts.*—The broken surfaces were calculated from the known thicknesses and widths of the test-specimens on the assumption that the depths of the notches were exactly 1 mm. It was therefore desired to ascertain whether, and to what extent, the actual surface differed from the calculated surface.

The dimensions of the broken surfaces of ten notched test-specimens, which had

been stretched to a slight extent and cut through with scissors, were measured by means of a microscopic scale. The mean values are summarized in Table III.

TABLE III

MEASURED AND CALCULATED VALUES OF BROKEN SURFACES

	Mixture A	Mixture B	Mixture C
Standard rings			
Measured (sq. mm.)	12.8	12.8	11.4
Calculated (sq. mm.)	12.0	12.0	12.0
Difference (in sq. mm.)	+0.8	+0.8	0.6
Difference (percentage of the calculated value)	+7	+7	+7
Test-strips			
Measured (sq. mm.)	8.1	8.8	8.3
Calculated (sq. mm.)	8.5	8.8	8.7
Difference (in sq. mm.)	−0.4	0	−0.4
Difference (percentage of the calculated value)	−5	0	−5

These measurements show that the true dimensions may deviate 5 to 7 per cent from the calculated dimensions. It should be noted that the deviations in the individual measurements were greater with test-strips than with standard rings.

(*d*) *Maximum Mutual Deviations of the Individual Measurements.*—These deviations were calculated from six determinations in various series of experiments. The results were calculated as percentages of the mean value, and are itemized in Table IV.

TABLE IV

MAXIMUM MUTUAL DEVIATIONS OF THE INDIVIDUAL MEASUREMENTS EXPRESSED AS PERCENTAGE OF THE MEAN VALUES

	Mixture A	Mixture B	Mixture C
Standard rings	12	10	9
Test-strips	24	17	27

The deviations are, of course, large, particularly in the case of the test-strips. This greater discrepancy with the strips is probably attributable to the fact that the side walls of the strips were convex, whereby the cutting was affected unfavorably and the deviations thereby increased.

In every case, it is highly advisable to make at least six individual measurements in every experiment.

On the basis of the results described, determinations of the resistance to tearing with standard rings and test-strips cut on all sides to a depth of 1 mm. can be accepted as a practical and efficient method.

The Position of the Optimum Tear-Resistance in Relation to the Optimum Tensile Strength

To establish the optimum tear-resistance in a series of cures, the method already developed was applied to mixtures having the compositions given in Table V. The mixtures were vulcanized for increasing lengths of time.

Mixtures I and II were "pure gum" mixtures, with a sharp optimum in the first case and a much less sharp optimum in the second case. Mixture III contained no free sulfur and had a very "flat" vulcanization curve. Mixture IV was a technical carbon black mixture. The results of the tear-resistance and tensile strength tests with standard rings are given in Table VI and are shown graphically in Fig. 9.

These results lead to the following conclusions:

1. The optimum tear-resistance was reached ahead of the optimum tensile strength in three of the four cases.

2. With mixtures I, III, and IV, the optimum tear-resistance and the optimum tear-resistance and the optimum aging coincided, the latter times having been found in other experiments to be 20, 15, and 30 min., respectively.

TABLE V

COMPOSITIONS OF THE MIXTURES

	I	II	III	IV
Rubber	100	100	100	100
Mineral rubber	..	..	..	8
Sulfur	5	3	..	3.5
Diphenylguanidine	1	0.6	..	1.25
Tetrone-A	..	..	1.5	...
Stearic acid	..	..	1	2
Machine oil	..	..	..	2
Zinc oxide	3	3	5	10
Carbon black	..	..	..	44.5
Temperature of vulcanization	147° C.	147° C.	135° C.	147° C.
Minutes of vulcanization	10, 20, 30, 40, 50.	15, 30, 45, 60.	15, 30, 45, 60.	15, 30, 45, 60, 75.

TABLE VI

TEAR-RESISTANCE AND TENSILE STRENGTH (IN KG. PER SQ. CM.) FOR THE VARIOUS STATES OF CURE

Time of Vulcanization (Min.)	Tear-Resistance	Tensile Strength	
10	39	137	Mixture I
20	67	195	
30	58	232	
40	27	207	
50	24	158	
15	33	155	Mixture II
30	51	159	
45	54	161	
60	51	162	
15	68	139	Mixture III
30	60	216	
45	55	216	
60	51	205	
15	105	174	Mixture IV
30	163	221	
45	160	235	
60	151	234	
75	138	234	

It would be desirable to carry on further experiments in this direction, but even now it seems likely that optimum tear-resistance coincides with the technically optimum cure which gives the best aging. If this is so, a tear-resistance test would be a simple method of determining the technically-best time of vulcanization.

Influence of Fillers on Tear-Resistance

A base mixture of 100 parts of rubber, 5 parts of sulfur, 1 part of diphenylguanidine, and 3 parts of zinc oxide, and this same mixture containing increasing propor-

tions of fillers, were tested for tear-resistance and tensile strength. The base mixture was vulcanized for 30 min.; the mixtures containing fillers were vulcanized for lengths of time which with 20 per cent by volume gave the best mechanical properties.

The results are recorded in Table VII and Fig. 10.

From the results in Table VII and Fig. 10 it is evident that:

1. Carbon black gave the highest tear-resistance at 30 per cent by volume and zinc oxide at 20 per cent by volume, whereas the highest tensile strengths were at 20 and 10 per cent by volume, respectively.

Worthy of note is the relatively sharp increase of the carbon black mixtures and the fact that 10 per cent by volume of zinc oxide improved the tear-resistance practically none at all.

TABLE VII

TEAR-RESISTANCE AND TENSILE STRENGTH WITH INCREASING PROPORTIONS OF FILLERS

	Percentage by Volume of Filler	Minutes of Vulcanization	Tear-Resistance (Kg. per Sq. Cm.)	Tensile Strength (Kg. per Sq. Cm.)
No filler	0	30	59	232
Carbon black	10	40	107	265
	20	40	163	266
	30	40	198	263
	40	40	168	231
Zinc oxide	10	30	60	254
	20	30	111	239
	30	30	96	202
	40	30	90	170
Devolite	10	30	23	231
	20	30	23	201
	30	30	26	172
	40	30	31	144
Whiting	10	30	27	228
	20	30	22	188
	30	30	24	167
	40	30	28	138

2. Devolite and whiting diminished considerably the tear-resistance, and there was practically no difference between small and large percentages of these two fillers.

In general the results agree well with those of Lefcaditis and Cotton.[1]

Practical Application of the Method

The method which has been described has already found practical application in the laboratory of the Government Rubber Institute at Delft, as shown by two cases which may be cited. In these applications of the method, it should be noted that the thickness of the test-specimens was not 5 mm. in every case. The depths of the cuts were regulated so that they were one-fifth to one-quarter of the dimension.

(*a*) *Rubber Covers of Conveyor Belts.*—High resistance to tearing is particularly important in the case of rubber covers of conveyor belts which are used in coal mines. To determine the tear-resistance of such covers, test-specimens were died out in both the longitudinal and transverse directions of the belts. These test-

specimens were buffed down on the rough side and were then incised on all sides. Since the prismatic part of the strips was about 2.6 mm. thick and 5 mm. wide, the strips were incised 1 mm. on the sides and 0.5 mm. on the top and lower sides.

The tear-resistance and tensile strength values of two different belts are shown in Table VIII.

TABLE VIII

TEAR-RESISTANCE AND TENSILE STRENGTH (IN KG. PER SQ. CM.) OF RUBBER COVERS OF CONVEYOR BELTS

Direction of Test-Specimen	Belt No. 1		Belt No. 2	
	Tear-Resistance	Tensile Strength	Tear-Resistance	Tensile Strength
Longitudinal	115	261	51	196
Transverse	45	216	34	186

It is evident from these measurements that the differences in tear-resistance between the longitudinal and transverse directions are considerable. On the contrary, differences in tensile strength between the two directions are only slight.

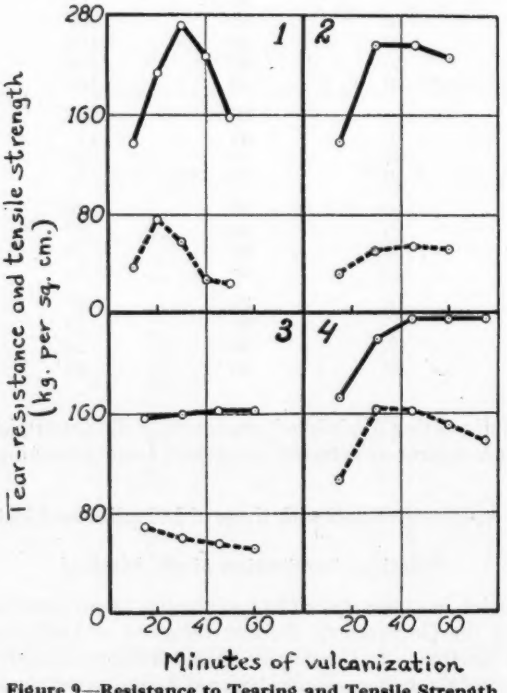


Figure 9—Resistance to Tearing and Tensile Strength in a Case of Step Vulcanization

Tensile strength ————
Tear-resistance - - - - - -

The difference in quality between belt No. 1 and belt No. 2 is more evident from the tear-resistance values than from the tensile strengths. The greatest differences between the individual measurements were 10 per cent of the mean value of

the belt with high tear-resistance and 20 per cent of the value of the belt with low tear-resistance.

(*b*) *Rubber Covers of Hose.*—High tear-resistance should be required of rubber hose which is used in workshops and other such places, and is subjected to rough treatment. To determine the tear-resistance of such hose, sections about 12 cm. long were cut off the cover, and these were cut all around at their center. The depth of the incision depended on the mean wall thickness of the rubber cover, and was 0.5 to 3.5 mm. for covers 1.4 to 5 mm. thick.

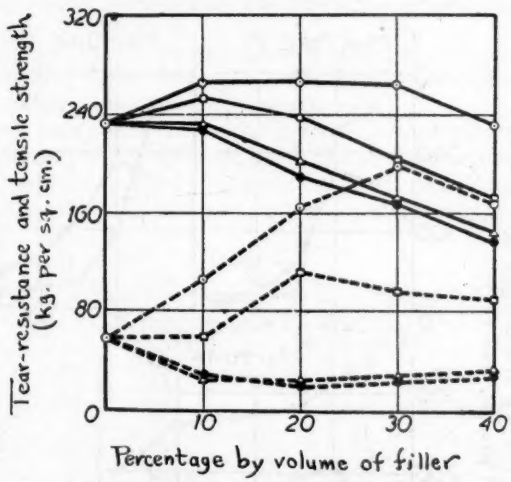


Figure 10—Resistance to Tearing and Tensile Strength with Increasing Proportions of Fillers

Figure 11—Elongation of a Normal Ring Specimen on the Pendulum Apparatus

Tear-resistance values from 27 to 170 kg. per sq. cm. were found for covers of various compositions, while the tensile strengths varied from 66 to 265 kg. per sq. cm. Here no relation between tear-resistance and tensile strength could be found. The greatest differences between individual measurements in each series were from 12 to 30 per cent of the mean value, depending on the quality of cover.

In the specification "Construction and Testing of Special Rubber Hose" of the Commission on Installation Problems, this method of testing is proposed, and a value of 75 kg. per sq. cm. is required as a minimum tear-resistance.

Determination of Tear-Resistance at High Speed

In many cases small particles of rubber are worn away at a high rate, *e. g.*, automobile tire treads when brakes are applied quickly. For this reason it is important to measure tear-resistance at high speeds. But still another reason led us to carry out experiments in this direction. In an earlier publication, van Rossem and Beverdam[10] described tensile tests at high speeds. These experiments were made with a Charpy pendulum apparatus. In continuing these experiments it was observed that standard rings showed various fissures, particularly where they

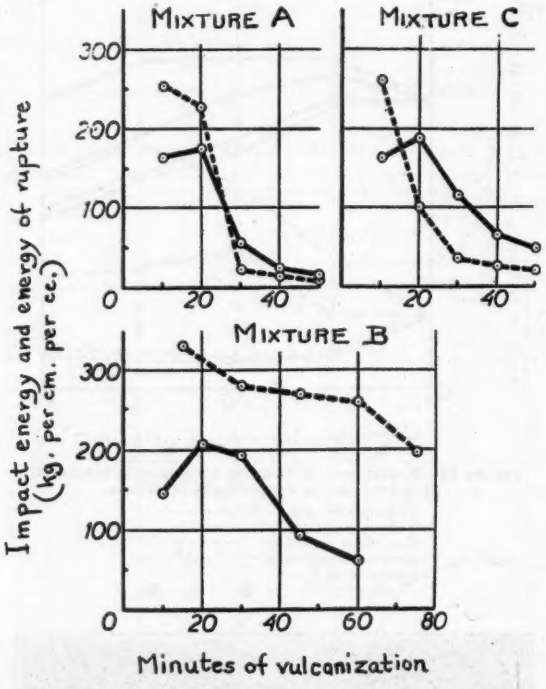


Figure 12—Tensile Strength and Tear-Resistance Tests by the Pendulum Apparatus
Energy of impact ————
Energy of rupture - - - - - - -

rubbed hard along the metal surfaces of the apparatus. It therefore seemed probable that the tensile tests of van Rossem and Beverdam were actually not tensile or breaking tests but rather tests of the resistance to tearing. A comparison of these earlier experiments with accurate tear-resistance tests at high speed therefore seemed advisable, and preliminary experiments with the pendulum apparatus have been carried out.

In this work, incised standard rings were fastened at right angles to the plane of the pendulum, as shown in Fig. 11, and then broken through by the pendulum beam at a velocity of approximately 4.8 meters per second. Under these conditions the rings were torn at one of the points where the incisions had been made.

To avoid any friction effect on the metal surfaces, these surfaces were lubricated each time with machine oil.

With incisions to a depth of 1 mm. on all sides, the torn cross sections were too small in area, so that the readings on the apparatus also were too small. Since an incision 1 mm. deep on one side gave about the same result as did incisions 0.5 mm. on all sides, the former method was chosen because of its relative simplicity. Accordingly the rings were incised to a depth of 1 mm. on one side only, as may be seen in Fig. 11.

As is known, the pendulum machine does not give the force, but rather the energy consumed in breaking through, which is calculated on a basis of cubic centimeters of the ring. The energy necessary to tear apart the incised rings is designated hereafter as the energy of rupture.

The thickness of an incised ring was assumed to be the original measured thickness minus the depth of the incision. Theoretically this assumption is not strictly correct, but it is satisfactory for comparative purposes.

The experiments were carried out with mixtures A, B, and C in Table I, except that in these experiments Thermatomic black was used in mixture B. The measurements, together with the energy values of the uncut rings (energy of impact at high velocity), are tabulated in Table IX and shown graphically in Fig. 12.

TABLE IX

ENERGY OF RUPTURE AND OF IMPACT OF STANDARD RINGS

Mixture	Minutes of Vulcanization	Energy of Rupture (Kg. Cm. per Cc.)	Impact Energy (Kg. Cm. per Cc.)
A	10	255	164
	20	226	173
	30	22	55
	40	14	23
	50	12	15
B	10	...	145
	15	330	...
	20	...	206
	30	280	193
	45	269	93
	60	259	62
	75	196	...
C	10	260	162
	20	100	186
	30	36	114
	40	25	65
	50	21	49

The results in Table IX and Fig. 12 make clear certain facts:

1. The impact energy curves show, as already known, optimum points, whereas the curves of the energy of rupture show no such optima. The mixtures vulcanized for the shortest lengths of time gave the maximum values for energy of rupture.
2. In several cases the energy of rupture was greater than the impact energy, even when the former was calculated on the whole volume of the ring.
3. The course of the energy of rupture curves of mixtures vulcanized more than 20 min., especially mixtures A and C, was very similar to that of the impact energy curves.

From these results and the other experiments mentioned, it may be concluded that the "tensile tests at high speed" of van Rossem and Beverdam were not really traction or tensile tests, but rather tearing tests. The fact that, in their work, mixtures vulcanized for the shortest times did not give the highest values may be

explained by a certain degree of tackiness of the undercured rings, which meant that the friction of these rings against the metal surfaces was greater than that of rings vulcanized for longer periods. Consequently, undercured rings tore on the metal surfaces and broke through sooner than did more highly cured rings.

It should be further noted that the importance of these so-called "tensile tests at high speed" as a method for the rapid determination of the technical optimum in a series of cures is enhanced rather than diminished by this explanation of their true character.

Influence of Fillers

The influence of fillers in the tear-resistance tests at high speed was studied with the same mixtures used in the first series of experiments on the tear-resistance. The results are given in Table X and Fig. 13.

TABLE X

ENERGY OF RUPTURE VALUES WITH INCREASING PROPORTIONS OF FILLERS

	Percentage by Volume	Minutes of Vulcanization	Energy of Rupture (Kg. Cm. per Cc.)
Filler	0	30	14
	0	40	10
Carbon black	10	40	36
	20	40	211
	30	40	206
	40	40	114
Zinc oxide	10	30	33
	20	30	39
	30	30	76
	40	30	91
Devolite	10	30	28
	20	30	54
	30	30	87
	40	30	81
Whiting	10	30	18
	20	30	20
	30	30	23
	40	30	23

The results in Table X and Fig. 13 show that when tearing was at high speed, mixtures containing 20 and 30 per cent by volume of carbon black gave the highest values. Zinc oxide gave considerably lower values, in fact even lower than did Devolite. Whiting gave the lowest values.

The most significant difference in the relation between the experiments at normal speed and those at high speed is that in the first case Devolite was without influence, whereas in the second case it had a reënforcing effect.

The experiments at high speeds are being continued.

Résumé

1. A method for determining tear-resistance is described, whereby standard rings and test-strips are incised to a depth of 1 mm. on all sides and are then pulled apart on a tensile testing machine operating at normal speed (50 cm. per min.).

2. The position of the optimum tear-resistance in relation to the optimum tensile strength for a series of cures was determined. The influence of increasing proportions of fillers on the tear-resistance was also investigated.

3. Examples of the practical application of the method to the testing of conveyor belts and hose are given.

4. Preliminary measurements of the tear-resistance of standard rings at high speed by means of a pendulum apparatus are described. These experiments show

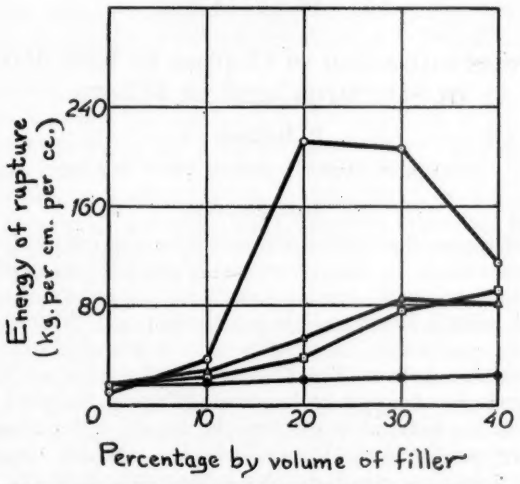


Figure 13—Energy of Rupture with Increasing Proportions of Fillers

Carbon black (thermatomic) ○——○
Zinc oxide □——□
Devolite △——△
Chalk ●——●

that previously published tensile tests at high speed resemble closely these new tear-resistance tests.

5. The effect of increasing proportions of fillers was also determined in the experiments at high speed.

Acknowledgment

The author wishes to thank A. van Rossem, Director of the Institute, for his encouragement and valuable criticism.

References

[1] Lefcaditis and Cotton, *Trans. Inst. Rubber Ind.*, **8**, 364 (1932).
[2] Lefcaditis, *Trans. Inst. Rubber Ind.*, **9**, 67 (1933).
[3] Talalay, *Kautschuk*, **9**, 82, 100 (1933).
[4] Kirchhof, *Ibid.*, **9**, 131 (1933).
[5] Clarke, *Trans. Inst. Rubber Ind.*, **10**, 80 (1934).
[6] Busse, *Ind. Eng. Chem.*, **26**, 1194 (1934).
[7] Farberov, *J. Rubber Ind.* (U. S. S. R.), **10**, 273 (1936).
[8] Behre, *Kautschuk*, **13**, 70 (1937).
[9] The width of the prismatic part was 5 mm.
[10] van Rossem and Beverdam, *Kautschuk*, **6**, 224 (1930).

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 14, No. 5, pages 80–84, May, 1938.]

Contributions to the Analysis of Rubber

III. Determination of Copper in Raw Rubber, in Mixtures, and in Fillers

P. Dekker

GOVERNMENT RUBBER INSTITUTE, DELFT, HOLLAND

1. Introduction

It is already well known that copper compounds have an extremely harmful effect on rubber articles. Since, however, very small quantities of copper are always present in fillers, in fact, in compounding ingredients in general and even in ordinary plantation rubber itself, it is not possible to manufacture a rubber article which is free of copper. In view of this, one must be content in each case with keeping the copper content within a certain allowable limit. However, it has been found that not only is the quantity of copper of decisive importance, but that still other factors play a part in the harmful effects brought about by the copper. Attention has been called repeatedly in the literature[1] to the fact that copper compounds which are injurious are those which dissolve in the rubber mixture. Nevertheless, it is certain that the harmful effects of copper depend not only on solubility but also on other factors. But since so little is known about this problem, nothing can be done for the time being except to regard any copper which may be found as injurious.

In the Netherlands Government Rubber Institute the permissible quantity of copper in rubber articles has been set at 0.001 per cent. Although with this percentage harmlessness is not guaranteed, it may still be expected that, with such small percentages of copper compounds, aging is not affected unfavorably.

The present work is concerned chiefly with methods for determining copper.

2. Determination of Copper in Inorganic Fillers

In any determination of copper in inorganic fillers, separation of the copper from other metals is an important consideration. This separation is carried out with hydrogen sulfide by the method of Ansbacker, Bemington, and Culp.[2] These investigators have shown that when the concentration of acid is 15 per cent by volume of sulfuric acid and the solution is heated to boiling, and when a few drops of nitric acid are added before treatment with hydrogen sulfide, small quantities of copper are completely precipitated. Sulfur, which separates when the nitric acid is added, functions as a carrier of the copper sulfide. This same method is outlined in detail in the Standards on Textile Materials of the American Society for Testing Materials.[3]

In further investigation of this method the following results were obtained:

1. 0.02 mg of copper is completely precipitated when the concentration of acid is 10 to 15 per cent by volume, and 0.3 cc. of nitric acid is added after passing hydrogen sulfide through for 3 min. When the nitric acid is added before treatment with hydrogen sulfide, separation of sulfur is at times incomplete. Without addition of nitric acid, 0.02 mg. of copper is not precipitated.

2. If the concentration of acid is lower, *e. g.*, 5 per cent by volume of sulfuric acid, 0.02 mg. of copper is completely precipitated if nitric acid is added after hydrogen sulfide has been passed through for 10 min. A disadvantage is that other metals as well are adsorbed by sulfur. The copper is finally determined with sodium diethyldithiocarbamate by the method of Callan and Henderson.[4]

Still other color reactions were investigated, but they were found to be less suitable, either because they were not sensitive enough or because the color changed too rapidly.

The dithizone reaction of Tischer and Leopoldi[5] was found to be very sensitive, but it is more tedious than the method of Callan and Henderson.

In view of the foregoing facts, the following method was employed for determining copper in inorganic fillers.

Five grams of sample are treated in a beaker (Griffin type of 400-cc. capacity) with 20 cc. of nitric acid (1.4 density) and heated on a water bath for 5 to 10 min.

Next, 10 cc. of sulfuric acid (50 per cent by volume concentration) are added, and the mixture is heated on a water bath until the odor of nitric acid has disappeared. The solution is taken up in 40 cc. of water, filtered through a Gooch crucible, and enough sulfuric acid is added to the filtrate to make the concentration of acid 10 to 12 per cent by volume. The filtrate is heated to the boiling point, and hydrogen sulfide is passed in until the solution has cooled. After passage of hydrogen sulfide for 3 min., 0.3 cc. of nitric acid (density 1.4) is added.

The precipitate is transferred to a filter (Schleicher and Schüll, No. 589, Blue band) and washed with 3 per cent acetic acid saturated with hydrogen sulfide. The funnel is kept covered with a watch glass during the filtration The filter is then incinerated in a white porcelain crucible, the ash is treated with a few drops of nitric acid (density 1.4), and the acid evaporated on a water bath.

The residue is dissolved in 3 cc. of 10 per cent ammonium hydroxide and the color of the solution is compared with the color of 0.2 mg. of copper sulfate ($CuSO_4.5H_2O$) dissolved in the same quantity of ammonium hydroxide. If the color of the sample is a paler blue than that of the copper sulfate solution, the copper content is less than 0.001 per cent.

If the copper content is greater than 0.001 per cent and no colorimeter is available, the same quantity of ammonium hydroxide solution is placed in a white porcelain crucible by means of a graduated 1-cc. pipette or microburette, and sufficient copper sulfate solution (1 gram of $CuSO_4.5H_2O$ per liter) is added to give the same color as that of the sample. In this case, addition of 0.1 cc. of copper sulfate solution indicates a copper content of 0.0005 per cent in the sample.

For precise determinations and with small quantities of copper, the residue is taken up in 5 cc. of 10-per cent ammonium hydroxide solution, is diluted with 40 cc. of water, and 10 cc. of 0.1 per cent aqueous sodium diethyldithiocarbamate are added. The yellow color is compared with a standard solution, containing 0.025 mg. of copper in the same volume, by means of a Wulf colorimeter. The sensitivity of this method is very great, and even 0.0001 per cent of copper can be determined with precision. In some cases it is necessary to amplify the procedure in the following way.

Iron and Chromium Compounds.—With these compounds hydrogen sulfide is oxidized, and iron and chromium are adsorbed by the resulting precipitate of sulfide. After incinerating the precipitate, the residue is taken up in a few cc. of hydrochloric acid and the acid is evaporated. The residue is then dissolved in sulfuric acid (10 per cent by volume concentration), and the precipitation by hydrogen sulfide is repeated.

Antimony Sulfide.—The determination of copper in antimony sulfide is carried out as follows.

Two grams of sample are mixed with 1 gram of ammonium chloride in a porcelain crucible, 10 cc. of concentrated hydrochloric acid are then added, and the acid is evaporated on a water bath. When the residue is almost dry, it is spread over the wall of the crucible and is heated further until all hydrochloric acid is evaporated. To complete the drying, the crucible is placed in a slanting position on a triangle, and its rim is heated with a small flame. The antimony and ammonium chloride are then driven off by heating with a flame, 3 cm. long. The residue is treated with 5 cc. of nitric acid (density 1.4) and 2 cc. of sulfuric acid (50 per cent by volume). After driving off the nitric acid, the copper is determined as already described. It was proved, by addition of a known quantity of copper oleate, that no copper is lost in the form of chloride.

Effect of the Incineration.—In view of the fact that in rubber articles copper is usually determined after incineration, experiments were carried out to ascertain whether any copper may be lost as a result of the inorganic fillers having been heated. Fillers were heated in a porcelain crucible for 15 min. with the full flame of a Teclu burner. Table I shows the copper content as determined directly and also after heating.

TABLE I

EFFECT OF HEATING FILLERS ON THEIR COPPER CONTENTS

Filler	Not Heated (Percentage)	Heated (Percentage)
Barytes	0.0007	0.0007
Barytes	0.0023	0.0030
Zinc oxide	0.0004	0.0004
Chalk	0.0002	0.0002
Kaolin	0.0007	0.0045
Kaolin	0.0070	0.0110
Kaolin	0.0023	0.0022
Kaolin	0.0004	0.0008
Kaolin	0.0005	0.0005
Kaolin (Devolite)	0.0003	0.0006
Kaolin (Devolite)	0.0003	0.0002
Colloidal clay (Wilkinite)	0.0002	0.0001
Colloidal clay (bentonite)	0.0001	0.0001

It is obvious from Table I that the percentages of copper were not reduced by the heat treatment, in other words, copper did not volatilize. With several of the samples of kaolin the values were actually higher, probably because of decomposition of silicate. It follows that, when kaolin is present in a rubber mixture, a higher percentage of copper may be found after incineration than would be expected from the copper content of the fillers. The determination of copper in rubber mixtures and similar products will be dealt with again later in this paper.

3. Determination of Copper in Raw Rubber, Organic Fillers, and Other Accessory Ingredients

The determination of copper in raw rubber, in organic fillers, and in other compounding ingredients, is carried out according to the following procedure.

Five grams of sample are incinerated in a porcelain crucible with a Teclu burner. Since in this incineration it is necessary to avoid a red heat, the ash in most cases contains particles of carbon.

The ash is treated with a few cc. of nitric acid (density 1.4) and 1 to 2 cc. of sulfuric acid (50 per cent by volume), and the nitric acid is then eliminated by heating

on a water bath. The residue is dissolved in sulfuric acid (10 per cent by volume) and is treated further as described in Section 2.

An investigation was then made of possible losses of copper during incineration. 0.0005 per cent copper in the form of various salts was added to samples of rubber powder and to potato flour before incineration. The results are summarized in Table II.

TABLE II

DETERMINATIONS OF COPPER IN THE ASH OF RUBBER POWDER AND POTATO FLOUR

	Percentage of Copper	
	Rubber Powder	Potato Flour
Blank	0.0016	0.0009
Blank + $CuSO_4$ (0.0005% Cu)	0.0021	0.0014
Blank + $CuCl_2$ (0.0005% Cu)	0.0022	0.0014
Blank + CuCl (0.0005% Cu)	0.0021	0.0013
Blank + Cu acetate (0.0005% Cu)	0.0022	0.0014
Blank + Cu tartrate (0.0005% Cu)	0.0021	0.0014

It is obvious from the determinations shown in Table II that no copper was lost during incineration in spite of the addition of copper salts, which led to the fear that there would be some losses.

A study was then made to determine whether, in the case of samples with low percentages of ash, separation by hydrogen sulfide can be dispensed with.

When the ash content amounts to only a few tenths of 1 per cent, as in first latex crepe and first latex sheet rubber, separation by hydrogen sulfide can be omitted in the procedure. The ash, which may not contain particles of carbon, is treated with a little nitric acid, the mixture is evaporated, the residue is dissolved in 2 cc. of 20 per cent sulfuric acid. After dilution with water, the solution is filtered, 7 cc. of 10 per cent ammonium hydroxide are added to the filtrate, and the copper is determined colorimetrically. This simplification of the procedure cannot, however, be applied indiscriminately to any sample.

If, after evaporation of the nitric acid, the ash is taken up directly in ammonium hydroxide, abnormally low percentages of copper are found, probably as a result of the presence of phosphates in the ash.

4. Determination of the Copper Content of Rubber Mixtures and of Vulcanizates

In the study of inorganic fillers it was shown that, when the samples of kaolin were heated, the percentage of copper soluble in nitric acid and in sulfuric acid increased. It therefore seemed desirable to find out how rubber mixtures containing kaolin behave in this respect. The direct determination of copper in mixtures was carried out in the following way.

Five grams of sample were dissolved in 30 cc. of nitric acid by heating cautiously on a water bath, and the solution was concentrated to about one-half its original volume. After addition of 10 cc. of sulfuric acid (50-per cent concentration by volume) the solution was heated further until the odor of nitric acid was no longer discernible. From this point the same procedure already described for inorganic fillers was followed.

Table III gives a few values of the copper content to show the comparative results obtained after incineration and by direct determination with a few samples of plastic packings.

TABLE III

COPPER CONTENTS AS DETERMINED IN THE ASH AND DIRECTLY IN THE SAMPLES

No. of Sample	Percentage from the Ash	Percentage Directly from Sample
18/34	0.0013	0.0008
37/34	0.0014	0.0007
39/34	0.0014	0.0007
372/33	0.0012	0.0006
407/33	0.0011	0.0006
429/33	0.0005	0.0005
432/33	0.0011	0.0008

The determinations recorded in Table III indicate a higher copper content in the ash. In the Netherland Government Rubber Institute the quality of plastic packings is judged by the copper content determined without incineration but directly on the sample. This is because the point of view is taken that copper compounds which are rendered soluble through decomposition by silicates are not originally present in harmful form.

If, however, the filler content of the rubber mixture is low, the copper content of the ash is determined because solution of 5 grams of sample in 30 cc. of nitric acid is difficult. In such cases, when the copper content is greater than 0.001 per cent, it is advisable, in order to be certain of the result, to repeat the determination with 2 grams of sample and to omit the incineration.

What has been said in connection with mixtures applies also to vulcanized rubber and rubber articles. In the Netherlands Government Institute, many determinations of the copper content of vulcanized rubber articles have been carried out according to this method.

5. Determination of Copper in Rubberized Materials

Various methods for the determination of copper in rubberized materials have been described, and these methods are essentially different from the solution method.

Ruthing[6] and also Kehren[7] evaporated a mixture of the ash, potassium chlorate, and concentrated hydrochloric acid two or three times. On the other hand, Kluckow and Siebner[8] heated the ash twice with nitric acid and concentrated sulfuric acid until the latter was eliminated. Durst[9] evaporated a mixture of the ash, nitric acid, and sulfuric acid twice. Kirchhof[10] carried out decomposition with concentrated nitric acid and incinerated the nitro compounds. The ash was digested with concentrated hydrochloric acid and dilute nitric acid. Rupp[11] destroyed the sample with nitric acid, sulfuric acid, and potassium sulfate; Smith,[12] with fuming nitric acid, sodium sulfate, and potassium sulfate, following which treatment the destruction was completed with sulfuric acid.

The chemical laboratories of the Harburger Gummiwarenfabrik Phoenix A.-G. at Harburg, and the Continental Gummiwerke A.-G. at Hannover, have jointly adopted the following method of determination.[13]

The ash from 20 grams of material is decomposed by fusion with a soda-potash mixture, and the fusion mixture is digested in hot water. The insoluble part is dissolved in dilute hydrochloric acid.

It is evident that with the methods just described, silicates are partially or wholly decomposed. In view of the fact that the copper content of kaolin is increased by heating the kaolin, it might be expected that the percentage of copper depends on this decomposition.

Comparative experiments were carried out by several of these decomposition methods. After decomposition, the residue was taken up in sulfuric acid (10-per cent concentration by volume), and the percentage of copper was determined by the procedure described in Section 2.

TABLE IV

EFFECT OF VARIOUS METHODS OF DECOMPOSITION ON THE DETERMINATION OF COPPER

	Percentage of Copper in			
Method	Kaolin	Kaolin	Rubberized Material	Camera Cloth
Institute (direct)	0.0009	0.0007	0.0009	0.008
Institute (in ash)	0.0024	0.0022	0.0010	0.0012
Ruthing and Kehren	0.0025	0.0020	0.0010	0.0022
Kluckow and Siebner	0.0012	0.0011	0.0009	0.0016
Soda + potash	0.015	0.016	0.0010	0.0038

It is quite evident from the analyses in Table IV that with the exception of the sample of rubberized material, different results were obtained by the various procedures. Particularly noteworthy are the very high results by decomposition with a soda-potash mixture. The total copper content is determined by this method. The already recorded fact that various investigators have obtained different values for the copper content of the same sample of rubberized material can be explained, among other ways, by the fact that decomposition of the copper compounds was effected in quite different ways.

Aside from differences in the methods used for decomposition, there is still another reason for differences in the results of copper determinations by different investigators. According to several of the methods described, copper is not separated from other metals by means of hydrogen sulfide, but the iron and aluminum are precipitated by ammonia and the copper in the filtrate is then determined colorimetrically. Doubtless the precipitate of iron and aluminum hydroxides retain amounts of copper which vary with the concentration of the copper present.

Kirchhof dissolved the precipitate by a few drops of concentrated hydrochloric acid, and precipitated it again by a few cc. of dilute ammonium hydroxide.

The experiments described below, which are summarized in Table V, indicate that the precipitate may hold considerable quantities of copper.[14]

The ash was dried in the presence of nitric acid and sulfuric acid by the method of Durst, was dissolved in dilute sulfuric acid, and ammonium hydroxide was added until the solution was alkaline. After heating on a water bath for a few minutes, the product was filtered, and the copper in the filtrate was determined by the dithizone method and also by sodium diethyldithiocarbamate. The results obtained with the ordinary hydrogen sulfide method are included for comparison.

TABLE V

		With NH_4OH	
Sample	Precipitation by H_2S (Percentage)	Dithizone (Percentage)	Na Diethyldithiocarbamate (Percentage)
Proofing	0.0009	0.0001	0.0002
Camera cloth	0.0012	0.0003	0.0003

Low results were also obtained with kaolin and clay.

A mixture of 5 grams of colloidal clay (bentonite), nitric acid, and sulfuric acid was evaporated twice and taken up in dilute sulfuric acid. After addition of am-

monium hydroxide solution until the reaction was alkaline, and after heating for a few minutes on a water bath, the product was filtered, and the copper in the filtrate and in the residue was determined by the method of the Netherlands Government Rubber Institute. Before evaporation, 0.005 and 0.001 per cent of copper were added. The total quantity of copper was also determined for comparison.

TABLE VI

	Total Copper (Percentage)	Copper in Filtrate (Percentage)	Copper in Residue (Percentage)
Sample	0.0002	absent	0.0002
Sample + 0.0005% Cu	0.0007	0.0001	0.0008
Sample + 0.001% Cu	0.0012	0.0002	0.0011

From the results in Table VI it is evident that most of the copper was retained in the precipitate. Further experiments showed that the precipitate of hydroxides might still contain a large quantity of copper, even after repeated precipitation with ammonium hydroxide. In a test with a sample containing 0.0012 per cent of copper, 0.0005 per cent of copper was found in the precipitate of hydroxide after a second precipitation. It should, however, be noted in this connection that the quantity of hydroxide precipitate was very large.

The results which have been described lead to the conclusion that, in order to determine copper correctly, separation by means of hydrogen sulfide is indispensable, and that separation by ammonium hydroxide is unsatisfactory.

What has been discussed with respect to rubberized materials, and in connection with the literature, which deals almost exclusively with rubberized materials, is also of importance in the determination of copper in fillers, rubber mixtures, and vulcanized rubber in general.

6. General Considerations in Connection with the Determination of Harmful Copper

In Section 1 it was remarked that the harmful effect of copper is governed by various factors. Since these factors are not completely understood, it becomes necessary to regard the total amount of copper found experimentally as harmful. Now it follows from the foregoing discussion that when the Netherlands Government Institute method is used, only copper compounds which are soluble in a mixture of nitric acid (density 1.4) and sulfuric acid (50 per cent concentration by volume) are determined. The Institute takes the point of view that copper compounds which do not dissolve in this mixture of acids are harmless. The results in Table IV show that this method gives the lowest values for the copper content. We are of the opinion that other methods are not to be recommended because repeated decomposition of silicates, etc., gives higher percentages of copper. One would not expect any harm from copper compounds which are occluded in silicates and can be determined only after decomposition by a mixture of soda and potash. Nevertheless, harmless as well as harmful copper compounds unquestionably dissolve in a mixture of nitric acid (density 1.4) and sulfuric acid (50 per cent by volume), and it is not impossible that by employing more dilute acids for dissolving the copper compounds the copper values would approach more nearly the content of actually harmful copper. A few determinations were made to throw light on this.

The percentages of copper in various fillers were determined:

1. By the ordinary procedure.
2. After six hours' extraction with 0.5 *N* acetic acid on a water bath (the filtrate was evaporated, the residue was taken up in sulfuric acid of 10 per cent con-

centration by volume, and the copper was precipitated by hydrogen sulfide).

3. After heating with oleic acid at 110° C. for 4 hours.

The oleic acid was dissolved in benzene, was filtered, and the filtrate was evaporated. The residue was incinerated, was treated with nitric acid, and evaporated, the new residue was taken up in sulfuric acid (10 per cent by volume concentration), and was treated as in Method (2) above.

Oleic acid was chosen because rubber contains about 1.5 per cent of a mixture of oleic acid and linoleic acid, and these acids probably dissolve the copper in the rubber.

The copper determinations are summarized in Table VII.

TABLE VII

DETERMINATION OF COPPER BY SOLUTION OF THE COPPER IN 0.5 *N* ACETIC ACID AND OLEIC ACID

Substance	Percentages of Copper		
	Nitric Acid and Sulfuric Acid (1)	0.5 *N* Acetic Acid (2)	Oleic Acid (3)
Kaolin 11/34	0.0007	0.0003	0.00005
Kaolin 11/34 heated 15 min.	0.0033	0.0002	absent
Kaolin 385/34	0.0070	0.0005	0.0002
Kaolin 1	0.0024	0.0012	0.0003
Barium sulfate	0.011	0.0035	0.0003
Barium sulfate	0.0003	absent	absent
Barium sulfate	0.0004	absent	absent
Barium sulfate	0.0027	0.0025	0.0013
Iron oxide	0.1420	0.035	0.013
Zinc oxide No. 1[a]	0.007	0.007	not determined
Zinc oxide No. 2[a]	0.0002	0.0002	not determined

[a] These samples of zinc oxide were dissolved in the calculated quantity of acetic acid, after which sufficient acetic acid was added to make the solution 0.5 *N* acid. With oleic acid a soap is formed by zinc oxide, and therefore a determination of copper was impossible.

The results in Table VII show that only part of the copper dissolved in 0.5 *N* acetic acid, except in the case of the sample of barium sulfate No. 4 and of zinc oxide, in which cases all copper dissolved. The quantity of copper which dissolved in oleic acid was smaller than that which dissolved in 0.5 *N* acetic acid, but in the cases of the sample of barium sulfate No. 4 and of iron oxide, the permissible quantity in rubber articles, as determined by the usual method, is exceeded.

It is difficult to judge the value of the experimental results, and this can be done only after extensive investigations. It should, however, be remarked that, in the case of raw rubber mixtures and vulcanized rubber, extraction with acetic acid and oleic acid can be made only with the ash, and therefore the results are less reliable, since changes take place during incineration. Furthermore, some copper compounds do not dissolve in dilute acids, but change under certain conditions, as in the case of copper sulfide, which may be oxidized to harmful copper sulfate. It is problematical whether it is going to be possible to develop a method for determining the true content of actually harmful copper, although it is not impossible that, by using less concentrated acids, solution of most of the harmless copper compounds can be avoided. In conclusion, some further results may be mentioned which have been obtained with the new copper coloring agents, Vulkanechtblau 5 G. F. Pasta, and Vulcatex Fast Blue B. S. These samples were analyzed in the same way as were the material recorded in Table VII. The results are summarized in Table VIII.

TABLE VIII

ANALYSES OF TWO NEW COPPER PIGMENTS

	Vulkanechtblau 5 G. F. Pasta	Vulcatex Fast Blue B. S.
Copper determined directly in the sample (in percentage)		
With nitric acid + sulfuric acid	1.7	4.8
With 0.5 *N* acetic acid	0.0021	0.0005
With oleic acid	0.0030	0.0036
Copper determined in the ash of the sample (in percentage)		
With nitric acid + sulfuric acid	5.1	5.6
With 0.5 *N* acetic acid	3.7	5.2
With oleic acid	0.9	2.1

The data in Table VIII show that considerable percentages of copper were found by the ordinary method. In view of the fact that these coloring agents have no harmful effect when used in rubber in practice, the ordinary method of determining copper gives too high results.

On the contrary, the quantity of copper according to the method using 0.5 *N* acetic acid and that using oleic acid is very small.

After incineration, considerable quantities of copper were found, even by the 0.5 *N* acetic acid and the oleic acid methods. Also the copper contents, determined by the ordinary method, were considerably higher after incineration. Since it has been found that the aging of rubber mixtures containing these copper pigments is satisfactory, it is obvious that the values obtained after incineration are valueless.

Résumé

The method used by the Netherlands Government Rubber Institute for determining copper in inorganic and in organic fillers, raw rubber, compounding ingredients, rubber mixtures, vulcanizates, and rubberized materials is described. Results which have been obtained in developing this method are discussed, and the following facts are pointed out.

Precipitation by hydrogen sulfide is recommended for the separation of copper from other metals. A definite concentration of acid and addition of nitric acid is necessary in this case. Heating at the temperature used for incineration of samples containing kaolin increases the values of the copper content.

The values for copper depend on decomposition of the ash, and consequently different percentages of copper were found by various methods of decomposition.

If, after evaporation with nitric acid, the ash is taken up in ammonium hydroxide solution, abnormally low values of the copper content are obtained.

The determination of the harmful forms of copper are then considered, and results obtained by extraction of the copper by means of 0.5 *N* acetic acid and oleic acid are described.

Acknowledgment

The author wishes to extend his sincere thanks to A. van Rossem, Director of the Netherlands Government Rubber Institute, for his valuable aid in the present work.

References

[1] Kluckow and Siebner, *Kautschuk*, **6**, 161 (1930). Ruthing, *Chem.-Ztg.*, **54**, 403 (1930). Kirchhof, *Kautschuk*, **3**, 257 (1927); **8**, 6 (1932). Kehren, *Melliand Textilberichte*, **13**, 533, 601, 652 (1932).

[2] Ansbacker, Bemington, and Culp, *Ind. Eng. Chem.*, Anal. Ed., **3**, 314 (1931).
[3] *Am. Soc. Testing Materials Standards on Textile Materials*, Designation D377-36T, **1936**, 197.
[4] Callan and Henderson, *Analyst*, **54**, 650 (1929).
[5] Tischer and Leopoldi, *Z. angew. Chem.*, **47**, 90 (1934).
[6] Ruthing, *Chem.-Ztg.*, **54**, 403 (1930).
[7] Kehren, *Melliand Textilberichte*, **13**, 653 (1932).
[8] Kluckow and Siebner, *Kautschuk*, **6**, 161 (1930).
[9] Durst, *Melliand Textilberichte*, **15**, 314 (1934).
[10] Kirchhof, *Chem.-Ztg.*, **56**, 296 (1932).
[11] Rupp, *Proc. Am. Assoc. Textile Col.*, **1930**, 215.
[12] Smith, *Proc. Am. Assoc. Textile Col.*, **1930**, 217.
[13] *Kautschuk*, **12**, 96 (1936).
[14] After completion of these experiments, an article by Kehren confirming this idea, appeared. Kehren removed iron compounds by means of citric acid (cf. *Melliand Textilberichte*, **18**, 313 (1937)).

[Reprinted from Industrial and Engineering Chemistry, Analytical Edition, Vol. 10, No. 2, pages 57–59, February 15, 1938.]

Preparation and Testing of Latex Compounds

J. W. MacKay

MONSANTO CHEMICAL COMPANY, RUBBER SERVICE LABORATORIES DIVISION, NITRO, W. VA.

WHILE the American Society for Testing Materials has standardized the conditions for the testing of crude rubber (*1*) compounds, there are no such accepted standards for testing latex compounds. Wohler (*7*) outlined the first constructive ideas on this subject. The object of this paper is to continue the work started by Wohler (*7*) and to suggest simple methods which will give reproducible results. Since latex is a variable material in itself and presents numerous difficulties in testing, it is necessary to employ certain precautions in the testing procedure which will be outlined below.

TABLE I. TYPICAL LATEX FORMULA

	Dry Basis	Wet Basis
Rubber as 60% centrifuged latex	100.0	166.6
Zinc oxide as a 50% dispersion	1.0	2.0
Sulfur as a 50% dispersion	1.5	3.0
Piperidine cyclopentamethylene dithiocarbamate (Pip-Pip)	0.5	0.5
Water to 54% total solid content	...	18.9

In Table I is given a typical latex formula which is employed throughout this paper with the one exception noted below. The zinc oxide and sulfur are added as aqueous dispersions, and the piperidine cyclopentamethylene dithiocarbamate as an aqueous solution. This formula was chosen on account of its simplicity and to eliminate as many variables as possible.

Preparation of Latex Test Films

The preparation of smooth uniform latex test films is necessary to obtain reliable results. It is generally customary to prepare the test films by: drying on glass trays in an oven at 45° C. (*3*), on unglazed tile at room temperature (*5*), or on glass trays at room temperature (*7*). These methods were not used here because the glass trays are difficult to clean; the use of the oven is impractical when comparing a series of compounds and may also cause prevulcanization at 45° C.; and the unglazed tile will remove water-solubles and will not produce a smooth surface on the film adjacent to the tile. Experiments proved that ordinary plane glass surfaces were satisfactory and much easier to prepare, the surface tension of any latex compound being sufficient to prevent its flowing over

the edges, if the film is not too thick and there are no large chips around the edges of the glass surface.

Therefore, ordinary window-glass plates 25.4 × 33 cm. (10 × 14 inches) are employed. These glass plates are placed on racks (Figure 1), leveled by means of screws, and protected from air currents by sheets of heavy single-nap cotton sheeting supported on a wood framework, forming a hood or chamber. A similar method has been suggested by Flint and Naunton (*4*).

The compound shown in Table I is allowed to stand about 1 hour to permit the escape of air bubbles, the foam is removed, and the compound is then stirred carefully to prevent possible stratification. Wohler's (*7*) use of burets was not followed because of their inconvenience and possibility of stratification; 250-cc. beakers were substituted. Two layers of fine cheesecloth (about 36 threads per inch, 14 threads per cm.) are fitted into the beakers, about 225 cc. of the compound are poured into this cheesecloth, and the cheesecloth is removed by withdrawing upward and over the side of the beaker, thus removing foreign material and breaking up all residual air bubbles. The 225 cc. of latex compound are poured on the glass plates, giving a dry film 1.52 mm. (0.060 inch) thick. Care must be taken to avoid

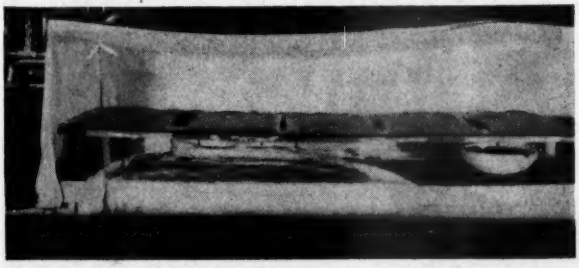


FIGURE 1

all air currents during the pouring and first 8 hours of drying. During this first drying period the relative humidity must be maintained at 60 to 70 per cent and the temperature must not be permitted to go below 21.2° C. (70° F.); after 8 hours the films have set sufficiently (although they may contain 15 per cent moisture) so as not to be affected by external conditions. The chamber is then opened for the free circulation of air to complete the drying process. In approximately another 8 hours the films have dried to a uniform color, which may be taken as an end point, and are removed from the glass plates and suspended to dry at room temperature.

The elimination of all air currents is essential from the time of pouring the film to the end of the setting period; otherwise a wrinkled surface will be obtained. Relative humidities below 60 per cent cause the formation of a surface skin over the wet film, resulting in deep surface cracks. Temperatures below 21.2° C. (70° F.) require a prolonged setting period and may result in the formation of wrinkles.

The absolute elimination of moisture in the uncured film is necessary to prevent retardation in air cures, but the presence of small percentages of moisture in the uncured film does not affect hot water cures. The drying period before cure should not be greater than 48 hours, as shown in Table II.

TABLE II. TESTS ON UNCURED FILM

Drying at 26.6° C. (80° F.)	2 Days		5 Days		9 Days	
	Kg./ sq. cm.	*Lb./ sq. in.*	*Kg./ sq. cm.*	*Lb./ sq. in.*	*Kg./ sq. cm.*	*Lb./ sq.in.*
Modulus at 500%	20.4	290	26.7	380	32.3	460
Modulus at 700%	62.5	890	78.8	1100	103.3	1470
Tensile at break	128.0	1820	151.3	2150	225.0	3200
Elongation at break, %	870		860		880	

The dried films are each divided into six sections of 7.35 × 13.97 cm. (3.25 × 5.5 inches) in order to obtain a range of cures, and the balance of the film is kept to determine the degree of prevulcanization at the time of testing. The curing of these films can be carried out at any desired temperature

FIGURE 2

or time. The usual procedure with this compound is to carry out cures for 0, 5, 10, 15, 20, 30, and 50 minutes in water at 100° C., or for 0, 10, 20, 30, 50, 90, and 130 minutes in air at 85° C. The films cured in water at 100° C. must be dried at room temperature for about 24 hours to allow them to shrink to a minimum thickness and the hot air–cured films are placed in a desiccator for about 24 hours to prevent their adsorbing moisture from the atmosphere.

The preparation of the latex test pieces is carried out in the manner outlined by the American Society for Testing Materials (*1*). The die for the preparation of the test pieces must have perfect cutting edges (*4*), giving a clean cut; otherwise short breaks and variable tensiles and elongations will be obtained. This is more evident in essentially pure-gum stocks than in stocks containing even 5 per cent filler on the rubber. In order to accomplish this, one die must be used only for pure-gum latex stocks, and this die should be sharpened frequently with a fine stone or razor hone.

The conditioning of the test pieces is markedly more important when testing latex compounds than when testing crude rubber compounds. Wohler (7) recognized the absolute necessity of controlling the humidity during the conditioning for testing of latex test pieces. Figure 2 shows a photograph of the device used for controlling the humidity for conditioning the test strips.

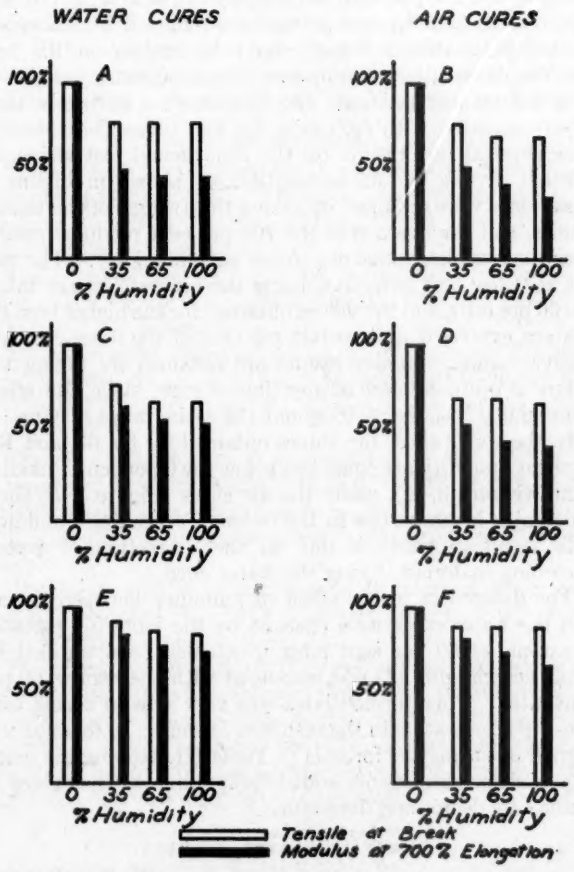


FIGURE 3. TEST RESULTS

Holes are punched in the end of the test pieces which are suspended on a steel wire, the wires being held in the cabinet by hooks attached to its upper framework. Lead trays 3.81 cm. (1.5 inches) deep containing concentrated sulfuric acid (100 per cent) fill the bottom as completely as possible, while air is circulated by the 15.24-cm. (6-inch) fan driven by a motor at approximately 400 r. p. m. The cabinet is constructed of a wood frame rabbeted to fit 6.35-mm. (0.25-inch) waterproofed Masonite board, the joints being sealed with several coats of shellac. The

door is fitted like a refrigerator door on soft-rubber-tubing gaskets.

In order to study the effect of humidity on latex test strips, eight films were dried as above. Four films were cured in water at 100° C. and four in air at 85° C., over the standard range of cures. Three test strips from each cure were suspended for 48 hours in desiccators containing various concentrations of sulfuric acid (*5*) so as to give humidities of 0, 35, 65, and 100 per cent, respectively (*6*), at 21.2° C. (70° F.) before testing. The test pieces were removed from the desiccator in quantities which could be broken on the test machine in less than 30 minutes, which exposure has shown no effect on physical tests and has shown a saving in time when compared with removing the test pieces individually. The physical test results on the conditioned test strips, as affected by the various humidities, are shown in Figure 3. These data were obtained by taking the average of the tensile results, and the average of the 700 per cent modulus results over the complete range of cures at each humidity. The values at 0 per cent humidity, being the highest (*7*), are taken as 100 per cent, and the values obtained for the higher humidities are expressed as a certain per cent of the 0 per cent humidity values. Similar results are obtained by taking the values at optimum cure or any time of cure, since the effect of humidity is similar throughout the entire range of cures.

In the water cures the values obtained for 35, 65, and 100 per cent humidity are equal but below the 0 per cent humidity value (Figure 3, *A*), while the air cures (Figure 3, *B*) show a decrease in properties in the order of ascending humidity. This result probably is due to the extraction of water-adsorbing materials during the water cure.

The differences in the effect of humidity between the air and the water cures were checked by the following method: A sample of 60 per cent latex which had been purified by triple centrifuging (*2*) was compared with the regular 60 per cent latex. This purified latex was very slow in curing with Pip-Pip acceleration in the standard formula; so this test was carried out using the formula in Table III, keeping the quantity of dispersing agents added comparable to that given in Table I by decreasing the sulfur.

TABLE III. LATEX FORMULA

	Dry Basis	Wet Basis
Rubber as 60% centrifuged latex	100.0	166.6
Zinc oxide as a 50% dispersion	1.0	2.0
Sulfur as a 50% dispersion	0.75	1.5
Piperidine cyclopentamethylene dithiocarbamate (Pip-Pip)	0.5	0.5
Di(benzothiazyl thiol) dimethyl urea	0.5	1.0
Water to 54% total solid content	...	18.9

Eight test films were prepared from each compound following the procedure given above. Four of each were cured in water at 100° C. and in air at 82° C. over a range of cures approximating those carried out on the formula given in

Table I. Test strips for the complete range of cures were conditioned as above and tested. The effect of humidity on the physical tests is shown in Figure 3, *C*, *D*, *E*, *F*. The regular 60 per cent latex shows the same general trend as the standard test formula in both water (Figure 3, *C*) and air cures (Figure 3, *D*). The purified 60 per cent latex shows much less effect of humidity on physical properties of the cured test strips and practically no difference between the water (Figure 3, *E*) and air cures (Figure 3, *F*). This is because the purification process has removed the greater portion of the water-solubles present in the latex. Latex purified by this centrifuging process is known to have a nitrogen content below 0.10 per cent and to be very much less hygroscopic.

Conclusions

Films should be prepared in an atmosphere free from air currents at 60 to 75 per cent relative humidity and at a temperature of 21.2° to 29.2° C. (70° to 85° F.) during the first 8 hours of the drying period.

These films should be suspended for complete drying for an additional 48 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before curing.

The water-cured films should be dried 3 hours in the open room followed by about 20 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before the preparation of test pieces.

The air cures are kept in a desiccator for about 24 hours at 0 per cent humidity and 10° to 15.5° C. (50° to 60° F.) before the preparation of test pieces.

The die for preparing test pieces must have perfect cutting edges.

Test pieces should be conditioned 48 hours at 0 per cent humidity and 21.1° C. (70° F.) before testing to obtain maximum tensile and modulus results.

The effect of humidity on physical test will be greater on normal latex, Revertex, and stabilized latex because of their increased water-soluble constituents which increase water adsorption. Good averages are obtained from three of four test strips broken, but for accurate work the average of the best four of six test strips should be taken.

Acknowledgment

The author wishes to thank the Monsanto Chemical Company for permission to publish this information, and the various members of the staff for helpful suggestions in its preparation.

Literature Cited

(1) Am. Soc. Testing Materials, D412-35T, p. 7 (October, 1935).
(2) Boggs and Blake, *Ind. Eng. Chem.*, 28, 1198 (1936).
(3) Du Pont Laboratory Report 181 (December 4, 1934).
(4) Flint and Naunton, *Trans. Inst. Rubber Ind.*, 12, 367 (1937).
(5) *Vanderbilt News*, 4, No. 5, 20 (1934).
(6) Wilson, J., *Ind. Eng. Chem.*, 13, 326 (1921).
(7) Wohler, *Ibid.*, Anal. Ed., 9, 117 (1937).

[Reprinted from Industrial and Engineering Chemistry, Analytical Edition, Vol. 10, No. 8, pages 428–431, August 15, 1938.]

Oxygen Pressure Aging

Improved Equipment

L. M. Freeman

THE B. F. GOODRICH CO., AKRON, OHIO

Since the introduction of the oxygen pressure-aging test by Bierer and Davis,[1] prevailing standard conditions for the test have been 70° C. (158° F.) and 300 pounds per square inch oxygen pressure. Various types of equipment have been used; usually the equipment has consisted of a pressure vessel immersed in a constant-temperature water bath to which is connected an oxygen supply. In the majority of instances the equipment has been difficult to operate and maintain for several reasons:

Immersion of pressure vessels in a water bath made handling difficult. Corrosion was a continuous source of trouble, causing "freezing" of cover bolts and making it difficult to obtain a leakproof oxygen seal between cover and vessel. This caused loss of oxygen.

Each time the pressure vessel was removed from the bath it was necessary to disconnect the oxygen supply and make the connection again when the test was started. This also caused loss of oxygen.

If more than one pressure vessel was connected to the oxygen supply and a safety released, the entire oxygen supply was exhausted.

The original pressure vessels were relatively large. Since the use of age resistors on a large scale, smaller units have been desirable in order to decrease migration of age resistors and eliminate erroneous results.

Some of these operation difficulties were outlined by Ingmanson and Kemp,[2] who also emphasized the importance of temperature control to obtain reproducible results.

It is the purpose of this paper to describe an improved oxygen pressure installation which avoids some of these difficulties.

Installation

Figure 1 is a chart showing one of two duplicate installations.

A crossover, *H*, connects the two circulating systems, so that if one of the constant-temperature supply tanks or circulating pumps must be repaired the entire oxygen system can be operated from the other supply. The pressure vessels, *A*, are jacketed and mounted on a steel table. The heat-transfer medium at present is water, which is maintained at constant temperature in tank *B* and circulated around the pressure vessels by circulating pump *C* through pipes *I*. The oxygen supply tanks, *D*, are on the opposite side of a brick wall, *E*, from the aging equipment. The instrument panel, *F*, is adjacent to the oxygen supply, so that the operator can read the instruments and shut off the oxygen pressure or temperature controls while on the opposite side of the brick wall from the pressure vessels. The oxygen supply is connected through reducing valves *G* and pipe *J* to the pressure vessels.

The pressure vessels are of two types:

1. Steel, inside diameter 5 inches and 11 inches high, jacketed so that a heat-transfer medium may be circulated around the vessel. The covers are fastened on with ten bolts.

2. Stainless-steel, 5.75 × 7 inches high (Fig. 2 is a drawing of the pressure vessel before jacketing), jacketed so that a heat-transfer medium may be circulated around the vessel. The cover consists of a circular disc which rests on a scaling ring and is held in place by a slide ring. An eighth turn of the slide ring locks it in place over the flange of the pressure vessel and then by means of ten set screws mounted through the ring, all impinging on the cover, a leakproof seal is easily obtained.

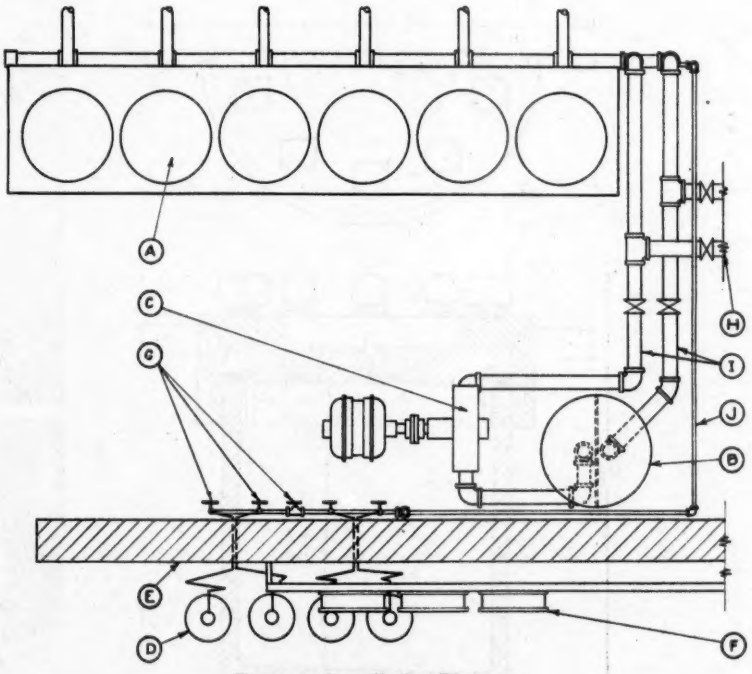


Figure 1—Installation Diagram

Figure 3 is a photograph of the heating system, showing how the electric immersion heaters are installed. The circulating pump and motor are shown in the lower left-hand corner. Figure 4 is a drawing of the heating tank.

The water returns from the jacketed pressure vessel through pipe *A*, is forced up past heaters *B* and over baffle plate *C*, down past temperature controller *D* and heaters *E*, through pipe *F* and circulating pump to the pressure vessels. Recording thermometers in pipes *F* and *A* indicate the temperature of the water before entering the pressure vessel jacket and upon return to the constant-temperature supply tank. To date the differential between these two recordings has been less than 0.5° C. (0.9° F.). The temperature bulb, *G*, actuates an automatic cutoff which is installed in the immersion heater circuit. This cutoff is adjusted to 77° C. (170.6° F.) when the operating temperature is 70° C. (158° F.) and is necessary in order to protect the apparatus in case the circulating system stops.

Figure 5 is a drawing and Fig. 6 a photograph of a pressure vessel mounted in place. In Fig. 5 the oxygen connection with safety mounting is shown at *A* and the water connections at *I*. The thermometer serves to show whether or not the water is circulating around the individual pressure vessel. It is possible to remove any individual pressure vessel very easily without interfering with the remainder of the system by closing the valves to the circulating system line and to the oxygen supply line, and disconnecting the unions.

The oxygen pressure is supplied from the tanks in Fig. 1 through the reducing valves shown in Fig. 7.

Between each pressure vessel and the oxygen supply line there is an automatic

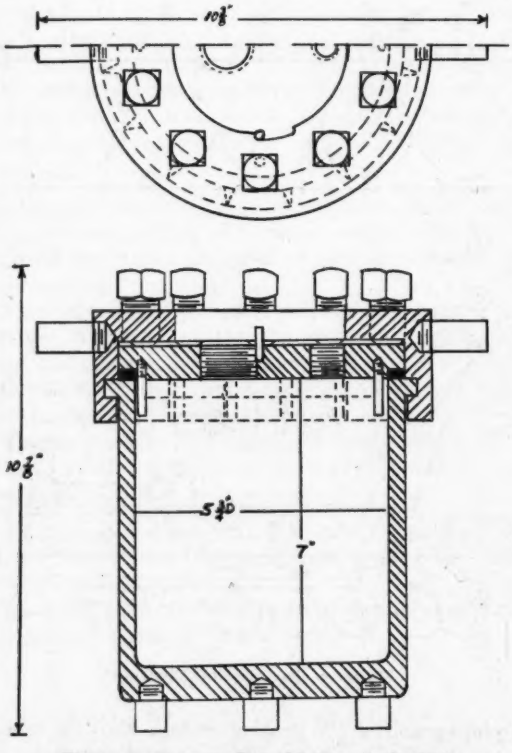
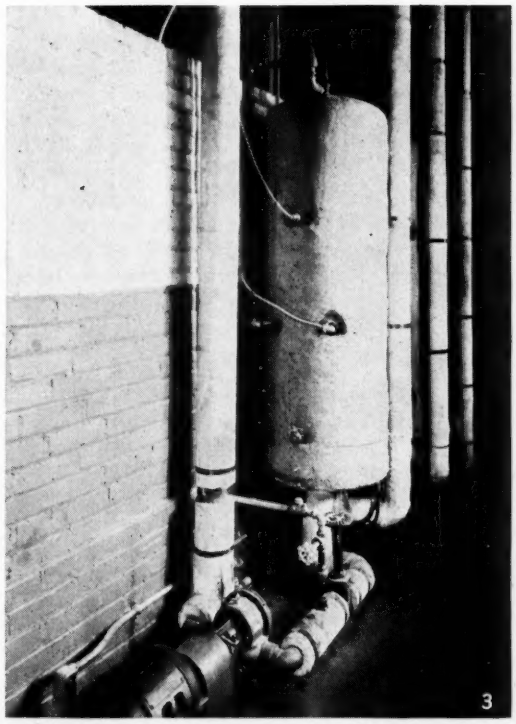
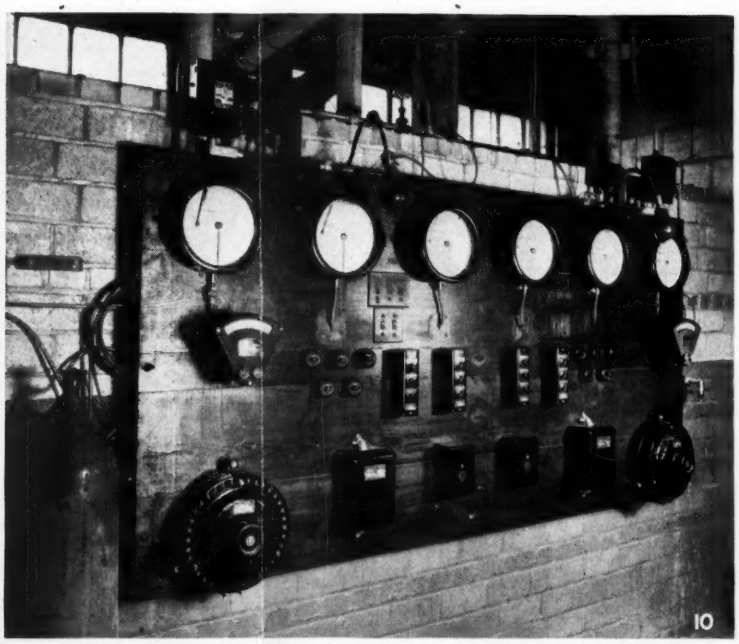
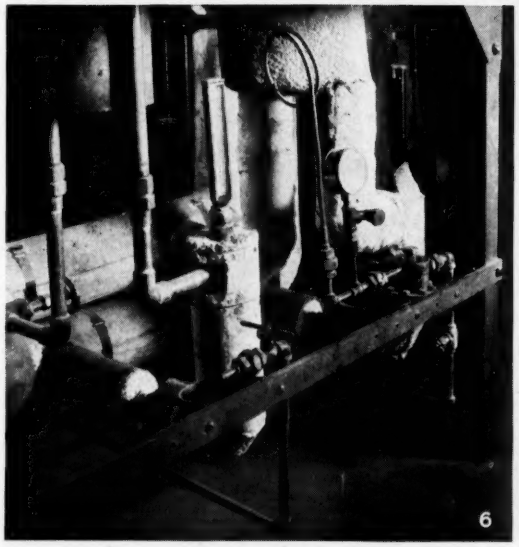


Figure 2—Pressure Vessel before Jacketing

cutoff valve shown at *B* in Fig. 5 and in detail in Fig. 8. The oxygen supply from the reducing valve enters the automatic cutoff valve through line *A*. The valve is actuated by a diaphragm, *D*, and by opening valve *C* the oxygen is released to the pressure vessel through line *G* and the pressure on both sides of the diaphragm is equalized through *F* and *B*. When the pressure is equal on both sides of the diaphragm, spring *H* opens valve *E;* valve *C* is then closed and if there is only a small leak through the pressure vessel system oxygen can feed through valve *E;* however, if pressure builds up in the pressure vessel and the safety releases, then the pressure is released through *F* on one side of the valve and the diaphragm immediately closes valve *E*. These valves operate so rapidly that it is impossible







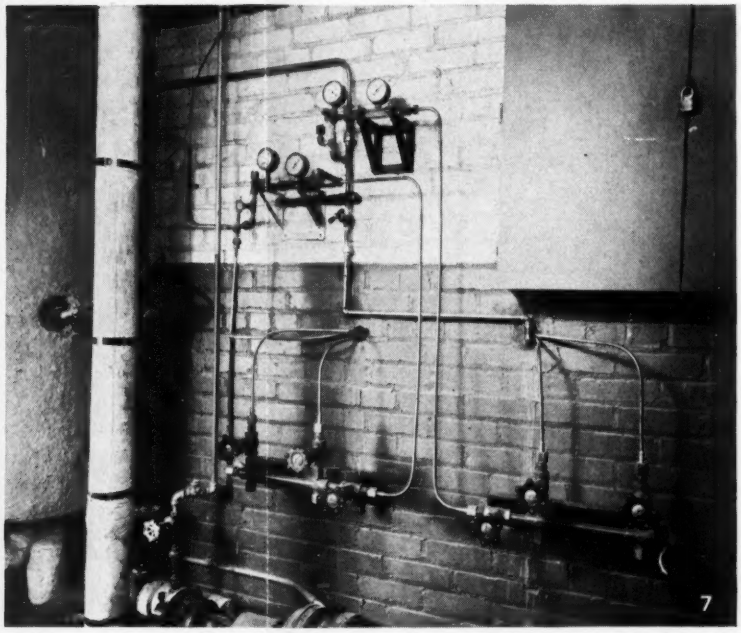
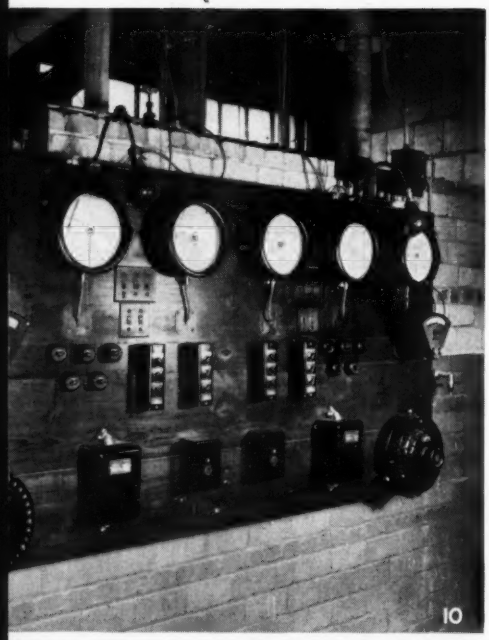
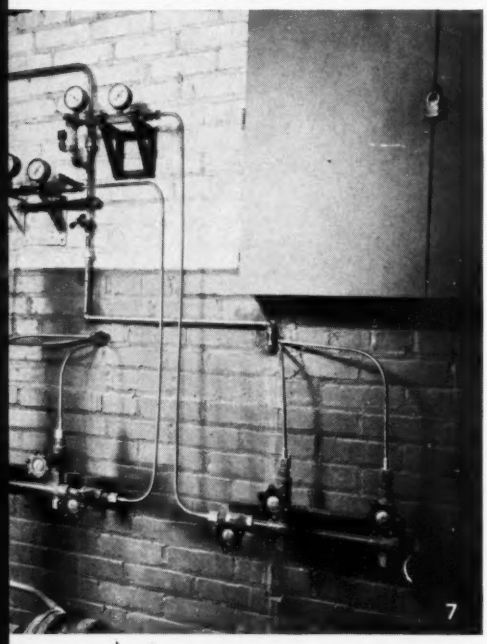


Figure 3—Heating System
Figure 6—Pressure Vessel in Place

Figure 7—Reducing Valves
Figure 10—Instrument Panel





ure 7—Reducing Valves
ure 10—Instrument Panel

to determine on the pressure-recording chart the time at which a safety has released.

Figure 9 illustrates the safety release—a disc of stainless-steel sheet mounted between tin discs in a compression seal. When the system is operating at 300 pounds per square inch the thickness of the disc is adjusted so that it releases at 350 pounds per square inch.

The instrument panel shown in Fig. 10 has two complete sets of instruments to record and control the operations of the two aging units.

Across the top of the panel are six recording instruments. The two pressure recorders are at the extreme ends; between these are the two pairs of temperature

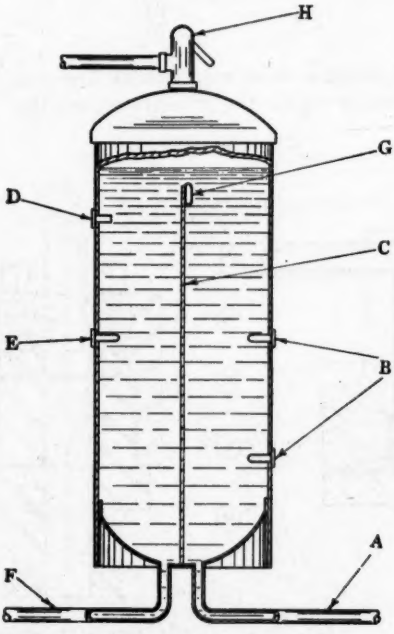


Figure 4—Heating Tank

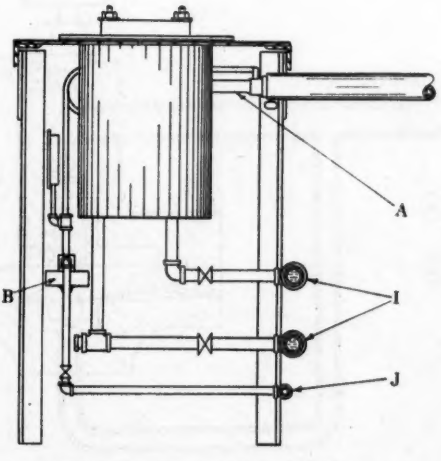


Figure 5—Pressure Vessel in Place

recorders connected to the return and outgo lines from the constant-temperature tanks. Below the pressure recorders are the temperature controllers for the constant-temperature tanks. These controllers actuate the heaters illustrated at *B* in Fig. 4. The upper row of the two sets of snap switches controls the heaters which are connected through the temperature controllers; the lower pair of the two sets controls the booster heaters, *E* (Fig. 4). The other two pairs of switches can be adjusted so that heaters *B* (Fig. 4) are connected separately or in any combination through the rheostats at the lower corners of the instrument panel to the thermometer controller or so that the heaters are connected direct to the thermometer controller. This makes possible a very accurate adjustment of the constant-temperature control. Just below each set of temperature recorders are lights in parallel with the heaters to show which heaters are in operation. Above the instrument panel and adjacent to the main supply line switches are the automatic cutoff switches which connect with bulb *G* in the constant-temperature tank.

Temperature inside Pressure Vessels

The original plans for the equipment specified that the pressure vessels be bolted to the metal tables, using a gasket to insulate the pressure vessel from the table. After the installation was made according to these plans the following temperatures were obtained inside the 5 × 11-inch pressure vessel:

Position inside Pressure Vessel (Inches from Top)	Temperature (° C.)	Water Temperature (° C.)
1	68.5	70
3	68.5	70
4	69.0	70
6	69.5	70
7	70.0	70
10	70.0	70

Similar readings inside the 5.75 × 7-inch stainless-steel vessels were low and more variable. In order to correct this variation within the pressure vessel, the tables were covered with Celotex and the pressure vessels then mounted in place. A wooden top was then fitted over the Celotex and around the lids of the pressure vessel covers. Covers of wood and Celotex were made to place over the pressure vessels and temperature readings inside the 5.75 × 7-inch stainless-steel vessels were as follows:

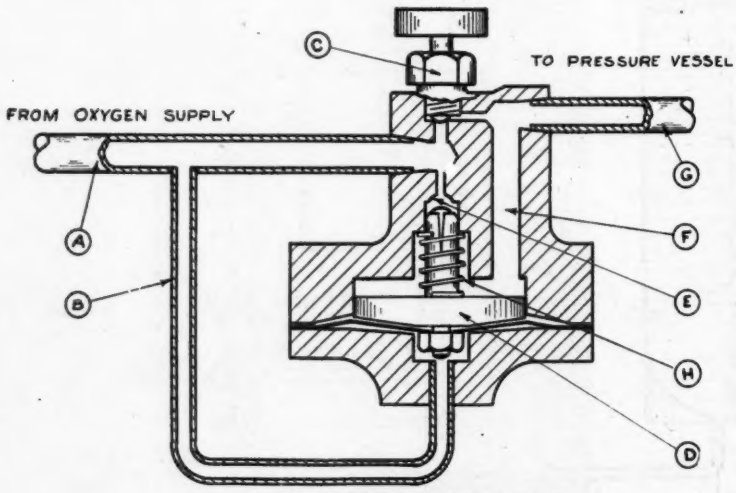


Figure 8—Automatic Cutoff Valve

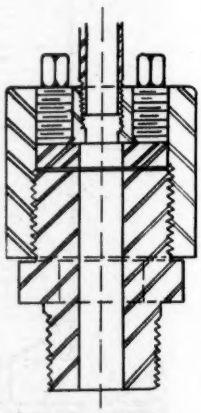


Figure 9—Safety Release

Position inside Pressure Vessel	Temperature (° C.)	Water Temperature (° C.)
1 Inch from top	69.5	70
1 Inch from bottom	69.5	70

With these data available it is possible to adjust the temperature of the circulating water to maintain 70° C. (158° F.) inside the pressure vessels.

Aging studies making use of the flexible facilities of this improved oxygen pressure-aging apparatus will be presented later.

Acknowledgment

Acknowledgment is made to N. E. Raber of the B. F. Goodrich Engineering Department, who designed the automatic cutoff valve (Fig. 8).

Literature Cited

[1] Bierer and Davis, *Ind. Eng. Chem.*, **16**, 711–17 (1924).
[2] Ingmanson and Kemp, *Ibid.*, **28**, 889–92 (1936).

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 14, No. 1, pages 49–64, June, 1938.]

Analysis of Organic Accelerators

J. G. Robinson

From the viewpoint of the works chemist, a knowledge of the qualitative and quantitative analysis of organic accelerators is desirable as a valuable supplement to a knowledge of their technical applications. Confusion or uncertainty as to the composition of a particular package of material may occur even in the best regulated factories; this may well prove to be an organic accelerator, and the chemist is expected to be able to give a decision in all such cases. Again, many accelerators are still sold under trade names and a knowledge of their chemical composition enables the chemist to use them in a more intelligent way, especially in predicting their vulcanizing characteristics in conjunction with other accelerators, and also in disposing of off-grade compounds by incorporation of a percentage in standard mixings.

Although the uniformity of qualtity reached by present-day suppliers of accelerators is of a high order, most works chemists wish as a matter of principle to institute some form of acceptance control. Tests in rubber are obviously desirable, but they take considerable time and require expensive plant; analytical methods, where available, enable some form of control to be exercised in cases where tests in rubber are impracticable owing to shortage of time or other considerations.

In 1923 an excellent and comprehensive account of the chemical examination of accelerators available at that time was given by Callan and Stafford (*J. Soc. Chem. Ind.*, **43**, 1T, (1924); *Third Year Book Inst. Rubber Ind.*, **1924**, 141). Further contributions have been made by von Wistinghausen (*Kautschuk*, **5**, 57, 75 (1929)), who worked out methods for estimating diphenylguanidine and mercaptobenzothiazole in vulcanized rubber, and by Shimada (*J. Soc. Chem. Ind. Japan*, **36**, 82B (1933)) who proposed to identify accelerators by their color reaction with cobalt oleate in benzene, supplemented by melting-point determinations. There have been other less important contributions, but in general the literature on accelerator analysis has lagged behind the literature on the technical applications of these materials.

The analysis of accelerators falls naturally into two divisions, qualitative and quantitative. Although quantitative methods must obviously be worked out independently for each accelerator or group of accelerators, it should be possible for the qualitative analysis of accelerators to be developed along lines well established for the analysis of organic substances in general, *i. e.*, determination of melting point and other physical constants of the accelerator and of suitable derivatives prepared therefrom. However, owing to the complex and unusual chemical substances which find application as accelerators, it frequently requires considerable investigation to work out suitable qualitative methods of identification. Difficulty may also be experienced in tracing melting points and other data which are scattered in the literature.

The present paper deals mainly with the qualitative examination of organic accelerators and describes methods which have been worked out for some accelerators or groups. A tabulated list of commonly used single chemical accelerators with melting points and other relevant data is given. A new method for the quantitative estimation of benzothiazyl disulfide is also described.

QUALITATIVE ANALYSIS OF ORGANIC ACCELERATORS

The first question to be decided is whether the accelerator is a single chemical substance or a mixture. This is readily observed by extracting the substance with a suitable solvent, isolating the extract, and comparing it with the residue for appearance and melting point.

Accelerator mixtures may contain free bases, such as diphenylguanidine, or free acidic accelerators, such as mercaptobenzothiazole, and these components may readily be removed by treatment with dilute acid or alkali, respectively. Mixtures of accelerators which are neither acidic nor basic are difficult to deal with. The components may be separated by fractional crystallization, but if this is unsuccessful it may be necessary to treat the mixture as a whole with a view to identification of decomposition products, such as carbon disulfide, aniline, secondary aliphatic amines, or aliphatic aldehydes. Each case must be treated on its merits; it is scarcely necessary to remark that a good knowledge of the analysis of single accelerators is essential for the elucidation of the composition of most of the mixtures.

If the accelerator under investigation is a single substance, the following scheme may be followed:

Appearance and Odor.—Indications as to identity are given by the odor of mercaptobenzothiazole and derivatives, dithiocarbamates, and some aldehydeamines.

Heat in Small Test Tube.—Volatile decomposition products such as carbon disulfide or ammonia may be recognized. Continue ignition and observe if there is any considerable inorganic residue.

Ash.—If the foregoing test indicates an inorganic residue, ash 1 gram of the material quantitatively and weigh and identify the residue. The following accelerators will leave inorganic residues: metallic salts of dithiocarbamates, xanthates, or mercaptobenzothiazole (residue may contain zinc, lead cadmium, or sodium); zincate of alpha-phenylbiguanide; dithiocarbamate accelerators deposited on a clay base.

Solubility in Water.—Test for solubility in water, hot and cold. Most accelerators are insoluble in water. The following are soluble: amine and sodium salts of dithiocarbamates; sodium isopropylxanthate; hexamethylenetetramine; aldehyde-ammonia; alpha orthotolylbiguanide; *p*-nitrosodimethylaniline (slightly); mercaptobenzothiazole (slightly soluble in hot water).

To Water Solution or Suspension Add a Little Concentrated Hydrochloric Acid and Warm.—Carbon disulfide may be evolved, indicating dithiocarbamates or xanthates. Guanidines dissolve readily, owing to formation of soluble hydrochlorides. Make the solution alkaline with caustic soda and warm. Dithiocarbamates give an ammonia-like odor of a secondary aliphatic amine, and guanidines are reprecipitated.

Warm Original Substance with Dilute (2 N) Caustic Soda Solution.—Mercaptobenzothiazole dissolves readily. Benzothiazyl disulfide and thiuram disulfides dissolve slowly, the latter giving a smell of secondary aliphatic amine. Acidify with hydrochloric acid; mercaptobenzothiazole is reprecipitated; a precipitate of mercaptobenzothiazole is also obtained from the solution of benzthiazyl disulfide in caustic soda.

Warm Original Substance with Concentrated Sulfuric Acid.—Practically all accelerators dissolve, many with decomposition evolving sulfur dioxide. If a dithiocarbamate or thiuram sulfide is suspected, dilute, make alkaline with caustic soda, and warm. An ammonia-like smell indicates dithiocarbamate or thiuram sulfide.

Test for Elements.—The decomposition products observed in the above reactions will generally render a test for nitrogen and sulfur superfluous. In cases of doubt,

make the usual tests. The test for nitrogen in presence of sulfur must be carried out carefully, otherwise the nitrogen may be missed. Accelerators may be classified into three groups according to the constituent elements, exclusive of carbon and hydrogen, as follows:

Nitrogen Only	Sulfur and Nitrogen	Sulfur Only
Guanidines	Dithiocarbamates	Xanthates
Biguanides	Thiuram sulfides	
Aldehydeamines	Mercaptobenzothiazole and derivatives	
Aldehydeammonia condensation products	Substituted thioureas	
p-Nitrosodimethylaniline		

Melting Point.—Determine the melting point of the material after crystallization; repeat if necessary. The melting points of most commercial accelerators without purification are up to 20° C. below figures recorded for the chemically pure materials, and even after repeated crystallization a low figure may still be obtained, due to the presence of isomers or impurities difficult to remove by crystallization. This applies particularly to the accelerators prepared from commercial piperidine. Consequently, although the melting point is a valuable guide to identification, it should be used only in conjunction with confirmatory tests. Table I gives melting points and other data on accelerators grouped according to their constituent elements.

Confirmatory Tests.—Sufficient indication should now have been obtained to narrow down the choice, and confirmatory tests should be applied as suggested in the notes to Table I.

TABLE I

DATA ON ACCELERATORS, GROUPED ACCORDING TO THEIR CONSTITUENT ELEMENTS

Melting points are taken from the literature, or determined by the author, and refer to pure or purified materials. Where data on purified accelerators is not available, melting points of commercial accelerators taken from suppliers' trade literature are given, these being indicated by the words "commercial product." The accelerators are arranged in order of increasing melting point within the groups.

Accelerators Containing Nitrogen Only

Guanidines (see Note 1).

146° C. triphenylguanidine $(C_6H_5NH)_2C{:}N.C_6H_5$. White crystalline solid, insoluble in water, soluble in alcohol and benzene. Picrate, melting point 181–181.5° C.

149° C. diphenylguanidine $(C_6H_5NH)_2C{:}NH$. White crystalline solid, insoluble in water, soluble in alcohol and benzene. Picrate, melting point 170° C. Compound with mercaptobenzothiazole, melting point 175° C.

175–176° C. diorthotolylguanidine. White crystalline solid, insoluble in water, soluble in alcohol and benzene.

Biguanides (see Note 1).

145–146° C. α-orthotolylbiguanide (material dried at 100° C.), $NH_2.C(:NH).NH.C(:NH).NH.C_6H_4.CH_3$. White substance, soluble in water, alkaline reaction, crystallizes from water with $0.5.H_2O$.

190° C. zinc α-phenylbiguanide, $[NH_2.C(:NH).NH.(NH.C_6H_5).C{:}N—]_2Zn$, white powder, insoluble in water and organic solvents.

Aldehydeamines (see Note 2).

These are liquids or resinous solids, having no definite melting point.

Alaehydeammonia condensation products (see Note 3).

96° C. *aldehydeammonia.* White solid, soluble in water, giving alkaline reaction.

280° C. *hexamethylenetetramine.* White crystalline solid readily soluble in cold water.

Nitroso compounds.

85° C. *p*-nitrosodimethylaniline; green solid, slightly soluble in water, soluble in most organic solvents, sparingly soluble in ether from which it crystallizes.

Accelerators Containing Nitrogen and Sulfur

Dithiocarbamates. (*a*) *Amine and alkali metal salts* (see Note 4).

81° C. diethylamine diethyldithiocarbamate, $(C_2H_5)_2N.C(:S)SH.(C_2H_5)_2NH$, white deliquescent crystalline solid.

132° C. dimethylamine dimethyldithiocarbamate, white crystalline solid, soluble in water.

158° C. sodium diethyldithiocarbamate; white solid, soluble in water; crystalline material melts in its water of crystallization about 98° C.

167–172° C. piperidinium pentamethylenedithiocarbamate, white crystalline solid soluble in water.

280–285° C. sodium pentamethylenedithiocarbamate (commercial product), white crystalline solid, soluble in water.

Dithiocarbamates. (*b*) *Metallic salts other than alkali metal salts* (see Note 4).

110° C. zinc di-*n*-butyldithiocarbamate, pale yellow solid, insoluble in water, sparingly soluble in alcohol from which it crystallizes.

175° C. zinc diethyldithiocarbamate (commercial product), white powder, insoluble in water, soluble in benzene.

222–225° C. zinc pentamethylenedithiocarbamate (commercial product), white powder, insoluble in water.

240–245° C. cadmium pentamethylenedithiocarbamate (commercial product), white powder, insoluble in water.

243–245° C. zinc dimethyldithiocarbamate, white powder, insoluble in water.

248–254° C. lead pentamethylenedithiocarbamate (commercial product), white powder, insoluble in water.

Dithiocarbamates. (*c*) *Esters* (see Note 4).

148° C. 2–4 dinitrophenyl dimethyldithiocarbamate, yellow crystalline solid, insoluble in water, sparingly soluble in alcohol from which it crystallizes.

183–185° C. diphenylcarbamyl dimethyldithiocarbamate (commercial product), yellow powder, insoluble in water, soluble in most organic solvents.

Thiuram sulfides (see Note 4).

70° C. tetraethylthiuram disulfide $[(C_2H_5)_2N.C(:S)S—]_2$, white crystalline solid, insoluble in water, soluble in alcohol and benzene.

109° C. tetramethylthiuram monosulfide, $(CH_3)_2N.C(:S).S.(:S).C.N(CH_3)_2$, yellow crystalline solid, insoluble in water, soluble in alcohol and benzene.

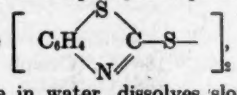
109° C. dipentamethylenethiuram monosulfide, pale yellow crystalline solid, insoluble in water, soluble in alcohol and benzene.

132° C. dipentamethylenethiuram disulfide, white crystalline solid, insoluble in water, soluble in alcohol and benzene.

150° C. tetramethylthiuram disulfide, white crystalline solid, insoluble in water, soluble in alcohol and benzene.

Mercaptobenzothiazole and derivatives (see Note 5).

180° C. mercaptobenzothiazole white crystalline solid (from water), slightly soluble in hot water, practically insoluble in cold water, soluble in aqueous alkalies, soluble in alcohol and benzene. Compound with diphenylguanidine, melting point 175° C., 2–4 dinitrophenyl compound, melting point 163° C.

178° C. benzothiazyl disulfide  , white crystalline solid (rectangular plates), insoluble in water, dissolves slowly in hot aqueous alkalies, fairly soluble in alcohol and benzene, readily soluble in chloroform and cyclohexanone.

Substituted thioureas.

151° C. thiocarbanilide, white crystalline solid, insoluble in water, soluble in alcohol and benzene.

Accelerators Containing Sulfur Only

Xanthates (see Note 6).

124° C. sodium isopropylxanthate (commercial product), pale yellow powder, soluble in water, insoluble in most organic solvents.

145° C. zinc isopropylxanthate (commercial product), $[(CH_3)_2CHO.C(:S)S—]_2Zn$, white powder, insoluble in water, soluble in warm benzene.

Note 1. Guanidines and Biguanides

The guanidines are organic mono-acid bases, readily soluble in dilute mineral acids, and are reprecipitated on making alkaline. A useful method of characterization is the determination of their molecular weight from their neutralization equivalent. 0.5 to 1.0 g. is dissolved in neutral alcohol, and titrated with 0.1 *N* hydrochloric acid, using as indicator bromphenol blue (change, blue to yellowish green).

The aryl biguanides may be characterized using the same method.

Note 2. Aldehydeamines

Simple aldehydeamine derivatives (Schiff bases) are obtained by interaction of one molecule of an aliphatic aldehyde with one molecule of an aromatic amine. Aldehydes used are formaldehyde, acetaldehyde, butyraldehyde, and heptaldehyde, and the amines used are aniline and *p*-toluidine. Formaldehyde and acetaldehyde also react in the ratio of one molecule aldehyde to two molecules of amine; *e. g.*, formaldehyde and aniline give methlenediphenyldiamine. Complex aldehydeamine derivatives are obtained by the further reaction of aliphatic aldehydes on the Schiff bases. The aldehydes used generally differ from those used in the preparation of the Schiff bases.

The author has used the following method for the qualitative detection of butylidineaniline. 16 g. of accelerator were refluxed with 50 cc. of concentrated hydrochloric acid and 50 cc. of water, for several hours. Hydrolysis was obviously incomplete, even after prolonged heating. The mixture was distilled, and to the aqueous distillate was added a saturated solution of 2–4 dinitrophenylhydrazine in 2 *N* hydrochloric acid. A reddish precipitate settled out on standing, and this was filtered and crystallized from alcohol, melting point 121° C. (melting point of butyraldehyde-2,4-dinitrophenylhydrazone, 122° C.). The residue in the flask was made alkaline and steam distilled, and aniline was detected in the distillate by the diazo-β-naphthol reaction, and preparation of the tribromo derivative (melting point 120° C.). It is probable that the other simple members of the series will be susceptible to a similar method of examination, bearing in mind that formaldehyde and acetaldehyde are very readily volatile.

The reagent 2–4 dinitrophenylhydrazine referred to above is very convenient for the detection of the aldehydes derived from rubber accelerators, and the following list of melting points will be found useful in this connection:

Aldehyde or Ketone	Melting Point of 2–4 Dinitrophenylhydrazone
Formaldehyde	166° C. (Campbell, *Analyst*, **61**, 391 (1936))
Acetaldehyde	168° C. (*Ibid.*)
n-Butyraldehyde	122° C.
n-Heptaldehyde	108° C. (*Ibid.*)
Acetone	126° C. (*Ibid.*)

Note 3. Aldehydeammonia Condensation Products

Aldehydeammonia and hexamethylenetetramine yield acetaldehyde and formaldehyde, respectively, on warming with dilute hydrochloric acid, and the aldehydes may conveniently be recognized by bubbling into a solution of the 2,4-dinitrophenylhydrazine reagent referred to in Note 2. Owing to the similarity of melting points of the derivatives from the two aldehydes, a mixed melting point with an authentic 2–4 dinitrophenylhydrazone will be necessary for definite characterization.

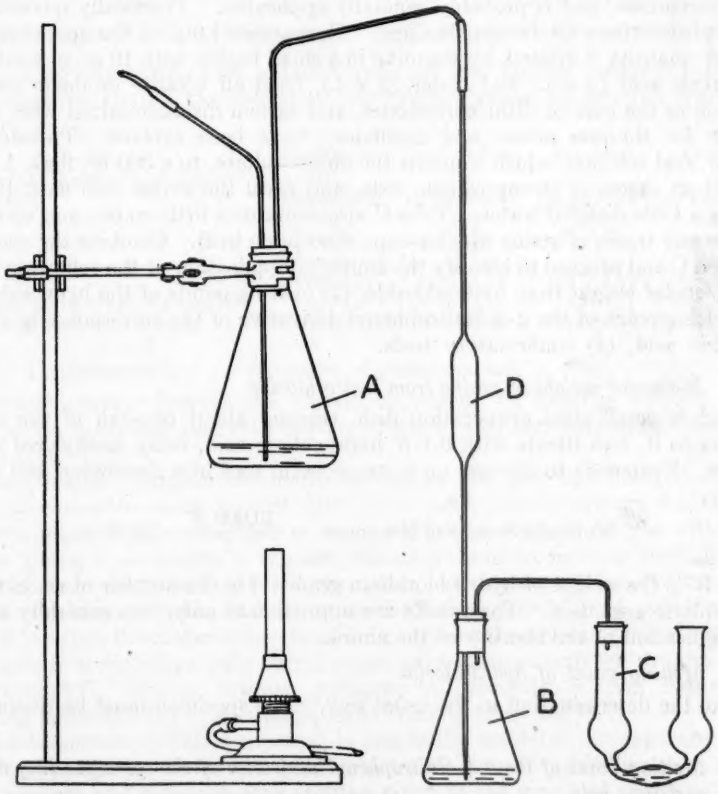


Figure 1—Apparatus for Collection of Gaseous Decomposition Products

Note 4. Dithiocarbamates and Thiuram Sulfides

These accelerators have as fundamental units a secondary aliphatic or heterocyclic amine and carbon disulfide. Amines used are dimethylamine, diethylamine, piperidine, and in one instance di-*n*-butylamine.

For the characterization of a substance in this group, it is necessary to identify the amine constituent, and this, taken in conjunction with solubility in water, metallic constituents if any, and melting point, will generally suffice for complete identification. Thus the sodium salts and the amine salts of the dithiocarbamates are soluble in water, but the rest of the group are insoluble. The insoluble members comprise those containing metallic constituents, that is, zinc, lead and cad-

mium dithiocarbamates and those free from metallic constituents, such as thiuram sulfides and dithiocarbamate esters.

For the identification of the secondary amine constituent of these accelerators, Callan and Stafford (*loc. cit.*) recommend the use of platinic chloride, but as this reagent is not generally available in works laboratories, it was thought desirable to work out alternative methods and these are described below.

The first step is to obtain an aqueous solution of the amine, and the following method is recommended. It has been found to be applicable to dithiocarbamates, thiuram disulfides, tetramethylthiuram monosulfide, and dinitrophenyl dimethyldithiocarbamate, and is probably generally applicable. Practically quantitative yields of secondary amine are obtained. Decompose 1.0 g. of the accelerator, or a larger quantity if diluted, by warming in a small beaker with 10 cc. of a mixture of sulfuric acid (3 vol.) and water (2 vol.), until all volatile products (carbon disulfide in the case of dithiocarbamates, and carbon disulfide mixed with sulfur dioxide for thiuram mono- and disulfides), have been evolved. Transfer the sulfuric acid solution, which contains the amine sulfate, to a 300 cc. flask A (Fig. 1), add an excess of strong caustic soda, and distil the amine into flask B containing a little distilled water. Tube C also contains a little water, and serves to remove any traces of amine which escape absorption in B. Combine the contents of B and C and proceed to identify the amine by application of the following tests: (1) molecular weight from hydrochloride, (2) melting points of the hydrochloride, (3) melting point of the 2–4 dinitrophenyl derivative of the corresponding dithiocarbamic acid, (4) confirmatory tests.

(1) *Molecular weight of amine from hydrochloride*

Weigh a small glass evaporation dish, transfer about one-half of the amine solution to it, and titrate with 0.1 *N* hydrochloric acid, using methyl red as indicator. Evaporate to dryness on a steam bath, cool in a desiccator, and weigh rapidly.

$$\text{Molecular weight of the amine} = \frac{10{,}000\ W}{t} - 36.5$$

where W is the weight of hydrochloride in grams; t is the number of cc. of 0.1 *N* hydrochloric acid used. The results are approximate only, but generally give a good indication of the identity of the amine.

(2) *Melting point of hydrochloride*

Make the determination in the usual way. The specimen must be reasonably dry.

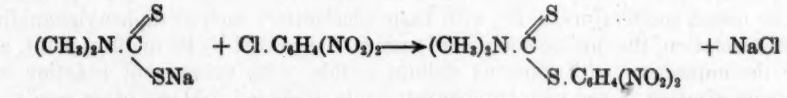
(3) *Melting point of the 2,4-dinitrophenyl derivative of the corresponding dithiocarbamic acid*

Titrate a portion of amine solution with 0.1 *N* hydrochloric acid. Alternatively the hydrochloride obtained in (1) may be redissolved in water. Add to the solution 0.1 *N* caustic soda solution equivalent to twice the hydrochloric acid titer. This liberates the amine and leaves one equivalent of caustic soda in excess. Add about 0.5 cc. of carbon disulfide and evaporate almost to dryness. The resulting product is the sodium salt of the corresponding dithiocarbamic acid.

$$(CH_3)_2NH + NaOH + CS_2 \longrightarrow (CH_3)_2N.\overset{\overset{S}{\diagup}}{C}\underset{\underset{SNa}{\diagdown}}{} + H_2O$$

Dimethylamine — Sodium dimethyldithiocarbamate

Take up the residue with aqueous alcohol, and then add excess of a saturated alcoholic solution of 2,4-dinitrochlorbenzene. The dinitro derivative may precipitate immediately or come down on rubbing the sides of the dish with a glass rod. The piperidine derivative tends to come out as an oil, but usually solidifies on standing. Crystallize the precipitate from alcohol and determine the melting point.



Sodium dimethyldithiocarbamate 2,4-Dinitrophenyl dimethyldithiocarbamate

The following results were obtained with the four amines prepared from commercial accelerators. Theoretical or authoritative values are given in brackets.

Test	Dimethylamine	Diethylamine	Piperidine	Di-*n*-butylamine
Molecular weight from hydrochloride	50 (theoretical 45)	76 (theoretical 73)	81 (theoretical 86)	135 (theoretical 131)
Melting point of the hydrochloride	128° C. Hygroscopic (170° C.)	215° C. (216° C.)	226° C. (237° C.)	Greater than 260° C. (No data)
Melting point of the 2,4-dinitrophenyl dithiocarbamate	149° C. (149° C.)	85° C. (No data)	92° C. (No data)	Viscous oil (No data)

(4) *Confirmatory tests for secondary aliphatic amines*

Dimethylamine.—Prepare the picrate by mixing an aqueous solution of the base and a saturated alcoholic solution of picric acid and determine the melting point (159° C.).

Diethylamine.—Prepare the hydrobromide as described for the hydrochloride and determine the melting point (219° C.). Alternatively prepare a solution of sodium diethyl dithiocarbamate as described under (3), and oxidize with 0.1 *N* iodine giving a precipitate of tetraethylthiuram disulfide, melting point 70° C.

Piperidine.—Perhaps the best confirmation is to isolate a few cc. of the liquid, dry over calcium chloride, and determine the boiling point. Pure piperidine boils at 105° C., but the material isolated from commercial accelerators without special attempts at purification boils over a range commencing about 90° C. and ending about 103° C. This is, however, sufficient to distinguish it from diethylamine (boiling point 55° C.) or di-*n*-butylamine (boiling point 158° C.).

Di-n-butylamine.—This compound is practically insoluble in cold water and a few cc. should be separated and dried for determination of the boiling point 158° C. Also prepare and determine the melting point of the zinc and cadmium dithiocarbamates by precipitation of the sodium salt of the dithiocarbamic acid, prepared in (3), with aqueous zinc sulfate or cadmium acetate, respectively; zinc dibutyldithiocarbamate, melting point 110° C.; cadmium salt, melting point 138° C.

For the complete identification of an accelerator of the dithiocarbamate or thiuram sulfide class, it is sometimes necessary to adopt quantitative methods as described by Callan and Stafford (*loc. cit.*), but the identification of the amine is a necessary preliminary.

Note 5. Mercaptobenzothiazole and Derivatives

The faint, though distinctive odor possessed by this group, generally provides the first clue to identification. Mercaptobenzothiazole itself is weakly acid in

character, and dissolves readily in dilute alkalies, giving soluble salts, which are in turn readily decomposed by mineral acids, reprecipitating the thiazole. Benzothiazyl disulfide is neutral in character, but is decomposed on boiling with aqueous sodium sulfide, giving a solution of the sodium salt of mercaptobenzothiazole. Further confirmation of benzothiazyl disulfide is given by microscopic examination of the crystallized material, the crystals taking the form of rectangular plates.

The 2,4-dinitrophenyl derivative of mercaptobenzothiazole is a component of some mixed accelerators, along with basic accelerators such as diphenylguanidine. After isolation, the dinitro compound may be recognized by its melting point, and by decomposition with aqueous sodium sulfide, with subsequent isolation and characterization of the mercaptobenzothiazole produced. Many other condensation products of mercaptobenzothiazole have been patented as accelerators, and if these are encountered it is interesting to note that Naunton, Baird, and Bunbury (*J. Soc. Chem. Ind.*, **53**, 127T (1934)) have shown that some of them are readily hydrolyzed by dilute alkali. This evidently affords a basis for their identification.

Note 6. Xanthates

On warming with sulfuric acid metallic xanthates are decomposed, giving carbon disulfide and an alcohol.

$$[(CH_3)_2CH.OC(:S).S—]_2Zn + H_2SO_4 \longrightarrow 2(CH_3)_2CHOH + CS_2 + ZnSO_4$$

Zinc isopropylxanthate — Isopropyl alcohol

The following method for the qualitative identification of zinc isopropylxanthate was worked out. Two grams of the material were ground into paste with water (it is very difficult to wet) and warmed with 50 cc. dilute sulfuric acid, using the apparatus shown in Fig. 1. A heavy yellow distillate of carbon disulfide was obtained and identified. To the sulfuric acid solution a few crystals of sodium dichromate were added, and flask B and tube C were charged with a saturated solution of 2,4-dinitrophenylhydrazine. On warming, a yellow dinitrophenylhydrazone was obtained, and this was filtered off and crystallized from alcohol. The melting point 125° C. corresponded to the 2,4-dinitrophenylhydrazone of acetone (melting point 126° C.), indicating that isopropyl alcohol was one of the original decomposition products by sulfuric acid. This, together with the melting point of the original accelerator, indicated zinc isopropylxanthate.

General Note on Manipulation

As many of the operations connected with accelerator analysis aim at preparing only sufficient of a pure derivative to enable a melting point to be obtained, it is frequently advantageous to work with very small quantities of material, thus utilizing the benefits of micro or semi-micro work, *e. g.*, rapid heating, cooling, and evaporation.

Crystallization of a tenth of a gram or less of material may be rapidly and efficiently effected by warming in a crystallizing dish with 2 or 3 cc. of solvent till dissolved, evaporating if necessary, cooling, and scratching the bottom of the dish till crystals separate. If the crystallizing solvent seems unsuitable, it is only a matter of a minute or less to evaporate the unsuitable solvent and try another. When filtering very small amounts of material, the usual Buchner filtering funnel is too large, as the crystals spread over the paper and are difficult to collect again. In such cases, filtration is preferably carried out on an ordinary conical filter paper, the crystals being washed into the apex. The paper is then opened out, the crystals

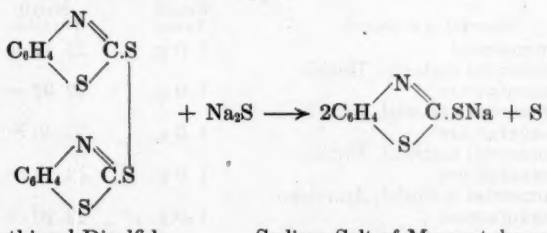
are removed with a flexible spatula, and dried by pressing on filter paper. Alternatively, filtration may be dispensed with, the crystals being manipulated to one edge of the dish by swirling and allowing to settle. The mother liquor is then carefully decanted by tilting the dish and the crystals are then removed with a spatula and dried on filter paper.

For the collection of gaseous decomposition products the simple apparatus shown in Fig. 1 has proved very efficient. Reagents are introduced through the bent tube in flask A, a small funnel being temporarily attached to the tube for this purpose. The bent tube may then be used for bubbling air through the apparatus or closed with a clip for distillation without an air current. Pipette D serves as a very useful safety device for prevention of "sucking-back" into the reaction flask, and also acts as an air condenser during the initial stages of distillation, frequently giving a clue to the distillation product. Thus, carbon disulfide condenses in oily droplets, diethylamine condenses as a smooth running liquid, and dimethylamine does not condense, owing to its low boiling point.

A small but useful improvement in melting-point technic has been made possible by the commercial development of oil-resisting synthetic rubber-like materials such as Neoprene. When liquid paraffin is used as a heating medium, the use of Neoprene rings in place of the usual rubber rings for attaching the melting-point tubes to the thermometer saves irritating delays due to the tube slipping into the paraffin.

QUANTITATIVE ESTIMATION OF BENZOTHIAZYL DISULFIDE

Benzothiazyl disulfide is a popular accelerator and is marketed alone and as a component of mixed accelerators. No method of quantitative estimation has yet been described. The author has found that when benzothiazyl disulfide is warmed with aqueous sodium sulfide, reduction takes place, and on acidification a quantitative yield of mercaptobenzothiazole is obtained. Based on this reaction, a method of estimation has been developed.



Benzothiazyl Disulfide Sodium Salt of Mercaptobenzothiazole

Reagents Required

Aqueous sodium sulfide, 200 grams of crystals dissolved in water and diluted to 1000 cc. (about 1.8 *N*).

Approximately 0.25 *N* caustic soda standardized by pure mercaptobenzothiazole (prepared by crystallizing commercial mercaptobenzothiazole from hot water). For standardization dissolve 1 g. of mercaptobenzothiazole in 50 cc. of warm neutral alcohol, cool, and titrate with caustic soda, using phenolphthalein; color change being from colorless to first trace of pink.

Method

Dissolve 1 gram of accelerator in 25 cc. of sodium sulfide solution in a 150-cc. tall beaker. Wetting and solution takes place most rapidly if the accelerator is

carefully brushed on to the surface of the liquid, previously heated just short of boiling point, avoiding contact with the sides of the beaker. Boil gently till dissolved, then cool and add, with continuous stirring, 25 cc. of 0.5 *N* hydrochloric acid and boil for about 10 minutes to remove hydrogen sulfide and to coagulate the sulfur. A little water should be used for washing down the sides of the beaker during boiling, but the total volume of liquid should not exceed 75 cc. Allow to stand overnight in a cool place. Filter off the precipitated mercaptobenzothiazole, wash with cold water till the washings give no further acid reaction with bromphenol blue (the total filtrate should not exceed 125 cc.). Use an ordinary filter funnel containing a paper pulp pad supported by a perforated disc. Filtration may be accelerated by gentle pump-suction, but it has been found to be more convenient to use the method described by Arnold and Ibbotson (*Steel Works Analysis*, Pitman); the stem of the funnel is cut off square and the filter so made that the portion below the pad is filled with liquid. Dry the precipitate on the filter at the pump, then invert over the original beaker, and blow down the stem to transfer the mercaptobenzothiazole with paper pulp to the beaker. Complete the transference by washing the funnel with hot neutral alcohol. To the beaker add 30 cc. of hot alcohol and boil gently for a few minutes to dissolve the mercaptobenzothiazole, then filter into a 300-cc. flask, using an ordinary conical filter and fast filter paper. Wash the filter and beaker thoroughly with hot alcohol, outside as well as inside, owing to the tendency of the alcohol solution to creep. Cool the alcoholic solution to room temperature, and titrate with 0.25 *N* caustic soda solution using phenolphthalein as indicator. With pure samples the end-point is colorless to pale pink, but many commercial samples yield a yellowish solution which gives a yellow-orange end-point, similar to the color change with methyl orange.

Results obtained using this method and samples from various sources were as follows:

Sample No.	Description of Sample	Weight Taken	NaOH Titration	Per Cent
1	Pure material	1.0 g.	23.47 cc.	99.5
2	Commercial material, British manufacture	1.0 g.	22.92 cc.	97.0
3	Commercial material, British manufacture	1.0 g.	23.40 cc.	99.1
4	Commercial material, British manufacture	1.0 g.	23.10 cc.	97.8
5	Commercial material, American manufacture	1.0 g.	23.20 cc.	98.4

The best of the commercial samples was No. 3, of British manufacture, and it is noteworthy that this sample was almost white rather than the usual yellowish color.

It is important that the caustic soda solution should be standardized with pure mercaptobenzothiazole, as a somewhat lower result will be obtained if, for instance, pure benzoic acid is used as a standard. The author has not succeeded in preparing a sample of mercaptobenzothiazole which titrates 100 per cent when caustic soda solution standardized by benzoic acid is used. Mercaptobenzothiazole, crystallized from hot water and dried at 100° C. titrated about 99 per cent; it is probable that the discrepancy is due to slight hydrolysis of the sodium salt of mercaptobenzothiazole.

As thiuram disulfide and substituted guanidines are possible components of accelerator mixtures containing benzothiazyl disulfide, tests were made to de-

termine whether accelerators of this type interfered with the estimation. One-gram samples of diphenylguanidine and tetramethylthiuram disulfide were treated as described for the estimation of benzothiazyl disulfide, but in both cases negligible titrations (about 0.1 cc.) of caustic soda solution were obtained. The method is therefore applicable in the presence of these accelerators, and will probably have wide application in the analysis of accelerator mixtures containing benzothiazyl disulfide.

Acknowledgment is made to Messrs. Ferodo, Limited, Chapel-en-le-Frith, for permission to publish this paper.

[Reprinted from the India Rubber World, Vol. 98, No. 2, pages 49–50, May 1, 1938.]

Apparatus for Evaluating Puncture Resistance

H. H. Bashore

VULCANIZED RUBBER COMPANY, MORRISVILLE, PENNSYLVANIA

In the development of improved compounds for products such as tires, inner tubes, conveyer belts, and hose, the need was felt of a quick and accurate test which would approximate the puncturing conditions these goods might receive in service. For such a test an apparatus was developed which provides for a puncturing pin to be pulled through the rubber sample, the pulling force being supplied by a vertical Scott tensile tester. The adaptation to the Scott machine (Fig. 1) eliminates the necessity of additional load-recording and extension-pulling apparatus.

Construction

The test apparatus, of which three views are shown in Fig. 2, is composed of two sections. The top section is a hollow tube through which the puncturing pin (Fig. 3A) travels downward in puncturing the sample (Fig. 3B), which is gripped firmly at the periphery between an internal shoulder on the tube and a sleeve (Fig. 3C) within a threaded cap (Fig. 3D) which screws on to the tube. Distortion of the test piece, while the screw cap is being tightened, is prevented by the inner sleeve which presses vertically against the specimen while the turning action is taken up by slippage between the sleeve and the cap. A horizontal pin is attached to the vertical puncturing pin to provide means for attaching the bottom tube section which pulls the pin downward. The hollow tube of the top section is slotted to allow vertical movement of this horizontal pin.

The bottom section consists of two members, a hollow tube, and an inner rod slotted to permit vertical movement of a horizontal pin permanently fixed in the tube to enable free relative movement of the two sections when changing test-specimens. The top of the hollow tube has a slotted hook arrangement which attaches to the horizontal pin of the top section. Both sections are provided with means of attachment to the pulling members of the Scott Tensile Machine. The weight of the top section is equal to the weight of the regular top clamp used in tensile tests, thus obviating correction of the dial reading.

A circular sample, $^3/_4$ inch in diameter and died out of the usual laboratory slab, is used for the test. In order to achieve a high-scale reading of the pulling force required, and therefore greater accuracy, many tests were made to determine the proper included angle of the point to be used to cause puncture. With test-specimens 0.065 inch in thickness or under, an included angle of 90 degrees was found to be quite satisfactory. However, with the usual specimen thickness of 0.100 inch, the angle is limited to 45 degrees.

Operation

Referring to Fig. 2, position A shows the apparatus before test with the cap containing the test-specimen tightly in place. The slotted hook of the bottom section is then attached to the horizontal pin of the top section, as shown in position B.

The tensile machine is started, and with this sliding tube arrangement the puncture pin is pulled down through the rubber specimen. Position C shows the apparatus after test, with the bottom section lowered and the puncture-point protruding through the cap. The entire test can be conducted in 45 seconds by a skilled operator.

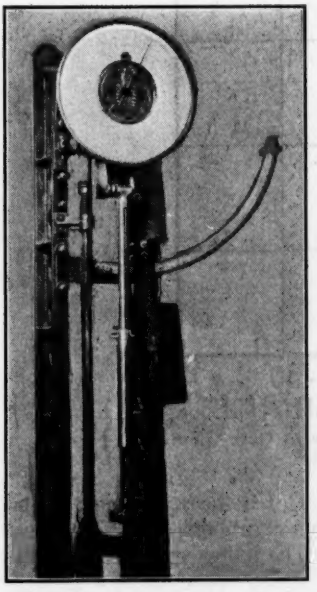


Figure 1—Apparatus Attached to Scott Tester

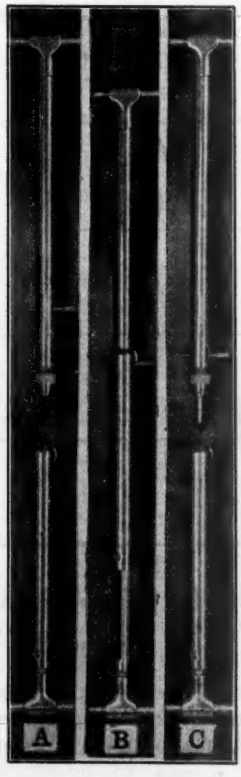


Figure 2—Three Positions during Operation

Figure 3—Puncturing Pin Assembly and Sample

The load or resistance to puncture is recorded on the dial of the Scott tester. By means of graduations on the top section and a feather edge at the upper end of the lower section, it is possible to obtain the deformation of the specimen at any point in the test. The degree of deformation at puncture is read when puncture is indicated by a popping sound. For calculation to a standard basis for com-

parison, it is assumed that the puncture resistance per inch of thickness equals the breaking or puncture load divided by the thickness of the test-specimen.

Utility of Test

There is in use at present a wide variety of tests for the evaluation of the physical properties of rubber compounds. In order to determine the relation, if any, of puncture resistance to standard physical tests, a series of compounds of widely different nature was tested for tensile strength, elongation, hardness, resilience, and puncture-resistance. The five compounds tested were as follows: compound

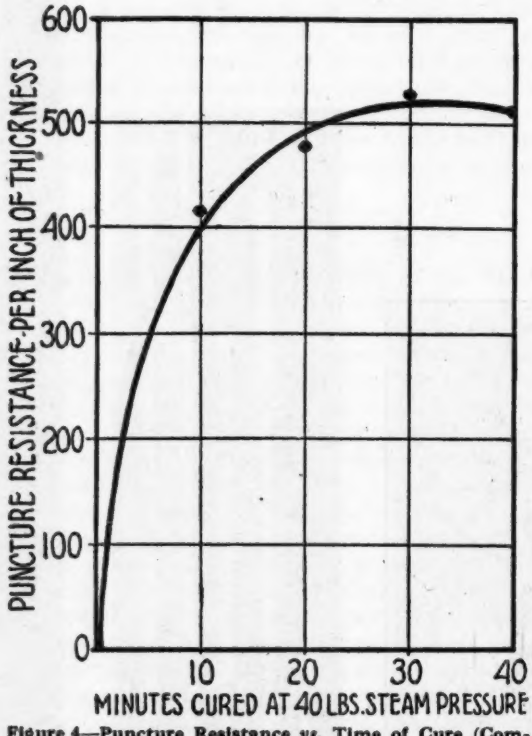


Figure 4—Puncture Resistance *vs.* Time of Cure (Compound A)

A, tire tread or belt cover; B, resilient pure gum; C, red sheet packing; D and E, oil-resisting hose tube stocks containing synthetic rubbers. All tests were conducted at 70° F. on samples of optimum cure. The following table shows the results.

Compound	A	B	C	D	E
Tensile strength	5000	4250	1100	1000	1750
Elongation at break	700	775	350	600	450
Shore hardness (type A durometer)	60	45	75	75	75
Resilience[a] at 70° F.	58	70	42	49	22.5
Puncture-resistance per inch of thickness	525	360	460	515	880

[a] Using improved rebound resiliometer described in RUBBER CHEM. AND TECH., Oct., 1937, pp. 820–826, the original form of which was presented in *India Rubber World*, Mar. 1, 1937, pp. 37–38, 51.

It is apparent, within the limited scope of these five compounds, that puncture-resistance as measured by this test bears no direct relation to the other physical properties, indicating that the new test will serve a definite purpose in evaluating resistance to puncture.

Another possible use for the apparatus is measuring the rate of cure. To indicate its application to this purpose, tests were taken on one compound. Figure 4 shows the puncture-resistance of compound A plotted against time of cure.

INDEX
RUBBER CHEMISTRY AND TECHNOLOGY
VOLUME XI, 1938

AUTHORS

Page

AMBROS, OTTO. A Study of the Formation of Rubber in the Plant ... 57
ARIANO, R. Compression Tests of Vulcanized Rubber ... 561
Tensile Tests with Flat (Straight) Test-Specimens ... 214

BAKER, H. C. The Concentration of Latex by Creaming ... 75
BARNETT, C. E. *See* Nellen, A. H.
BASHORE, H. H. Apparatus for Evaluating Puncture Resistance ... 740
BLOW, C. M. The Deposition of Rubber on to Textile Fibers ... 545
BONDY, C., AND FREUNDLICH, H. Proteins in Preserved Hevea Latex ... 601
BONGRAND, J.-CH. Difficulties in the Thorough Impregnation of Textiles with Latex ... 538
BRILL, R., AND HALLE, F. Rubber-like Behavior of an Artificial Substance (Oppanol) when Irradiated with X-rays ... 687

CHURCH, H. F., AND DAYNES, H. A. The Falling-Weight Impact Test for Ebonite ... 224
CLARK, GEORGE L., WOLTHUIS, ENNO, AND SMITH, W. HAROLD. X-Ray Diffraction Patterns of Sol, Gel, and Total Rubber when Stretched, and when Crystallized by Freezing and from Solutions ... 32
CLEWS, C. J. B., AND SCHOSSBERGER, F. Structure of Stretched Rubber ... 510
COKER, F. J. *See* Davey, W. S.
COTTON, F. H., AND WESTHEAD, J. The Activating Influence of Metallic Oxides on Vulcanization in the Presence of Organic Accelerators ... 331

DANIEL, F. K., FREUNDLICH, H., AND SÖLLNER, K. Coagulation of Latices by Polar-Nonpolar Liquids ... 87
Stability of Ficus Elastica Latex ... 624
DAVEY, W. S., AND COKER, F. J. The Preparation of Latex and Determination of Quality ... 459
DAVIES, B. L. *See* Wright, J. M.
DAYNES, H. A. *See* Church, H. F.
DEKKER, P. Contributions to the Analysis of Rubber. III. Determination of Copper in Raw Rubber, in Mixtures, and in Fillers ... 706
DOGADKIN, B. A., AND KOVARSKAYA, B. M. Colloidal and Chemical Investigation of Different Brands of Latex; Natural Latex, Jatex, Revertex, Revertex-T, and Revultex ... 630
DOSTAL, H. The Influence of the Temperature on the Crystallization of Rubber ... 348
DUBINKER, YU. *See* Frumkin, L.
DUFRAISSE, CHARLES. A Manometer for Measuring the Oxidizability of Rubber ... 268
———, AND ÉTIENNE, ANDRÉ. The Influence of Vulcanization on Oxidizability in Relation to Aging ... 282
DYER, J. W. W. *See* Stevens, H. P.

ECK, LEO. History of Rubber. Franz Carl Achard's "Experiments on Elastic Resin" ... 653
Contribution to the History of Latex ... 482
ELIEL, K. W. Effect of Organic Accelerators on the Temperature Coefficient of Vulcanization ... 101
ÉTIENNE, ANDRÉ. *See* Dufraisse, Charles.

FERRY, JOHN D. *See* Spence, D.
FIELD, J. E. *See* Gehman, S. D.
FORD, T. FOSTER. The Properties of Rubber Cements ... 142
FORMAN, D. B. *See* Garvey, B. S., Jr.
FREEMAN, L. M. Oxygen Pressure Aging. Improved Equipment ... 722
FREUNDLICH, H. *See* Bondy C.; Daniel, F. K.
FRUMKIN, L., AND DUBINKER, YU. Investigation of the Thermal Conductivity of Rubber ... 359

GARVEY, B. S., JR., AND FORMAN, D. B. Chemistry of Soft Rubber Vulcanization. Reversion and Non-Reversion in Low-Sulfur Compounds ... 680
GEER, WILLIAM C. Research Coöperation in the Rubber Industry ... 263
GEHMAN, S. D., AND FIELD, J. E. Colloidal Structure of Rubber in Solution. Effects of Precipitants ... 663
GLEICHENTHEIL, S., AND NEUMANN, W. The Gough-Joule Effect in Vulcanizates ... 508
GROTE, H. WALTER. Control Tests of the Uniformity of Carbon Black in Its Manufacture ... 598
GUTH, EUGENE. Observations on the Viscosity of Rubber Solutions ... 676

HAGGOOD, B. J. Bonding ... 169
HALLE, F. *See* Brill, R.
HAUSER, E. A. A Contribution to the Early History of India Rubber. François Fresneau (1703–1770) ... 1
HEDVALL, J. ARVID, AND LARSSON, ATLE. The Influence of the Crystallographic Transformation of Sulfur on the Course of Vulcanization ... 317
HENNE, ALBERT. *See* Midgley, Thomas, Jr.
HINTENBERGER, H., AND NEUMANN, W. Behavior of Raw Rubber when Stretched Isothermally ... 647

	Page
JONES, FORDYCE. Improved Packing of Rubber	439
KEMP, A. R. Composition and Structure of Hevea Latex	394
See also Taylor, R. L.	
KHERASKOVA, E., AND KORSUNSKAYA, E. A New Method for the Direct Determination of Rubber. A Preliminary Communication	438
KORSUNSKAYA, E. *See* Kheraskova, E.	
KOVARSKAYA, B. M. *See* Dogadkin, B. A.	
KRATKY, O., PHILIPP, H., POSNANSKY, K. W., AND SCHOSSBERGER, F. A New Transformation Product of Rubber	661
LARSSON, ATLE. *See* Hedvall, J. Arvid.	
LEDUC, HENRI. Some Applications of High-Frequency Electric Currents to the Latex Industry.	570
LEWIS, W. K., SQUIRES, LOMBARD, AND NUTTING, ROBERT D. Mechanism of Rubber Vulcanization with Sulfur	107
LOW, RODOLFO. Azo Dyes Derived from Rubber	515
LUCAS, FRANCIS F. Ultraviolet Microscopy of Hevea Rubber Latex	405
MCCLELLAN, PAUL D. *See* Park, C. R.	
MACKAY, J. W. Extraction of Water-Soluble Accelerators in Water Cure	591
Preparation and Testing of Latex Compounds	716
MEYER, KURT H. Fusion Curves of Rubber and Gutta-Percha	658
MENADUE, F. D. Highly Reactive Sulfur or the Reaction of Ammonia and Sulfur Chloride in Rubber Solutions	92
MIDGLEY, THOMAS, JR., HENNE, ALBERT L., AND RENOLL, MARY W. Natural and Synthetic Rubber. XVIII. The Protein from Natural Rubber and Its Amino Acid Constituents	5
MORSS, HENRY A., JR. An X-ray Study of Stretched Rubber	352
NELLEN, A. H., AND BARNETT, C. E. Processing Characteristics of Rubber Compounds — Effect of Pigment Particle Size and Surface	585
NEUMANN, W. *See* Gleichentheil, S.; Hintenberger, H.	
NUTTING, ROBERT D. *See* Lewis, W. K.	
OBERTO, S. The Fluorescence of Vulcanization	310
PARK, C. R., AND MCCLELLAN, PAUL P. Flocculation of Pigment in Carbon Black–Rubber Mixtures	575
PARKINSON, D. *See* Tidmus, J. S.	
PELZER, H. Kinetic Theory of the Elasticity of Rubber	644
PETROV, K. *See* Zelde, O. A.	
PHILIPP, H. *See* Kratky, O.	
PHILIPPOFF, W. Comparative Viscometric Studies of Solutions of Crepe Rubber and of Buna	372
PLAIZIER, J. A. *See* van Rossem, A.	
POPHAM, F. J. *See* Stevens, H. P.	
POSNANSKY, K. W. *See* Kratky, O.	
PUMMERER, RUDOLF, AND RICHTZENHAIN, HERMANN. Rubber. XVIII. Various Ozonides of Rubber and the Problem of the Existence of the Primary Ozonides of Harries	7
RACHNER, MANFRED. Estimation of the Stability of Rubber Solutions	558
RENOLL, MARY W. *See* Midgley, Thomas, Jr.	
RICHTZENHAIN, HERMANN. *See* Pummerer, Rudolf.	
ROBERTS, K. C. The Components of Hevea Latex. Part II. Seasonal Variations in the Composition of Typical Seedling Latex	445
Part III. Analyses of Plantation Rubber and of Creamed Latices	452
Part IV. The Effect of Ammoniation on Latex	455
ROBINSON, J. G. Analysis of Organic Accelerators	728
ROSSEM, A. VAN, AND PLAIZIER, J. A. Studies of the System Latex-Colloidal Clay	433
ROWE, J. W. *See* Stevens, H. P.	
SAGER, THERON P. Permeability of Organic Polysulfide Resins to Hydrogen	163
SCHMIDT, ERNST, AND STAMBERGER, PAUL. Some Properties of Rubber Latex	479
SCHOSSBERGER, F. *See* Clews, C. J. B.; Kratky, O.	
SCOTT, J. R. Behavior of Ebonite towards Organic Liquids	147
SHIMADA, KEICHI. Studies of Organic Accelerators. XVI. Part 4. Detection and Analysis of Organic Accelerators. Detection of Guanidine Accelerators in Vulcanized Rubber	531
Part XVIII. Part 6. Detection of Dithiocarbamate Accelerators in Vulcanized Rubber	533
Part XIX. Part 7. Detection of Thiuram Accelerators in Vulcanized Rubber	535
SLEPUSHKINA, E. Rapid Detection of Accelerators	210
SMITH, W. HAROLD. *See* Clark, George L.	
SÖLLNER, K. *See* Daniel, F. K.	
SPENCE, D., AND FERRY, JOHN D. Enhanced Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds	47
SQUIRES, LOMBARD. *See* Lewis, W. K.	
STAMBERGER, PAUL. *See* Schmidt, Ernst.	
STARKWEATHER, HOWARD W., AND WALKER, HERBERT W. Water Resistance of Neoprene	383
STERN, H. J. The Marking of Uncured Rubber Mixes	441
STEVENS, H. P., DYER, J. W. W., AND ROWE, J. W. Purification and Concentration of Rubber Latex with Special Reference to Dialysis	423
——, AND POPHAM, F. J. Oxidation Products of Rubber: Rubbone	523
TAYLOR, R. L., AND KEMP, A. R. Sorption of Water	485
TIDMUS, J. S., AND PARKINSON, D. Some Applications of the Microscope to Rubber Technique	197
VAN HARPEN, N. H. The Kinetics of the Coagulation of Latex of Hevea Brasiliensis and the Separation of the Hydratant Acid	60

	Page
VAN WIJK, D. J. Determination of the Resistance of Vulcanized Rubber to Tearing	689
VESTER, C. F. Creaming of Heavea Latex by Colloids	608
WIEGAND, WILLIAM B. pH Properties of Colloidal Carbon	187
WALKER, HERBERT W. *See* Starkweather, Howard W.	
WESTHEAD, J. *See* Cotton, F. H.	
WOLTHUIS, ENNO. *See* Clark, George L.	
WRIGHT, J. M. The Vulcanization of Rubber with *m*-Dinitrobenzene	131
——, AND DAVIES, B. L. Vulcanization of Rubber in the Presence of meta-Dinitrobenzene	319
ZEÏDE, O. A., AND PETROV, K. D. The Mechanism of the Action of Vulcanization Accelerators. Derivatives of Mercaptobenzothiazole. II. The Transformation of Mercaptobenzothiazyl Sulfide	97
ZIEGLER, KARL. The Polymerization of Butadiene and the Production of Artificial Rubber	500

SUBJECTS

	Page
Accelerators. Analysis of Organic	728
Effect on Temperature Coefficient of Vulcanization of	101
Detection of Dithiocarbamate	533
Thiuram	535
Guanidine	531
in Water Cure. Extraction of Water-Soluble	591
of Vulcanization. Mechanism of Action of	97
Organic	331
Rapid Detection of	210
Studies of Organic	531
Achard's "Experiments on Elastic Resin"	653
Activating Influence of Metallic Oxides on Vulcanization in the Presence of Organic Accelerators	331
Aging. Influence of Vulcanization on Oxidizability in Relation to Oxygen Pressure	282
Oxygen Pressure	722
Amino Acid Constituents. Protein from Natural Rubber and Its	5
Ammonia and Sulfur Chloride, Reaction of	92
Ammoniation. Effect on Latex of	455
Analysis of Organic Accelerators	728
Rubber. III	706
Apparatus for Evaluating Puncture Resistance	740
Artificial Rubber. Polymerization of Butadiene and Production of	501
Azo Dyes Derived from Rubber	515
Behavior of Ebonite towards Organic Liquids	147
Raw Rubber when Stretched Isothermally	647
Bonding	169
Buna. Comparative Viscometric Studies of Solutions of Crepe Rubber and of	372
Butadiene and Production of Artificial Rubber. Polymerization of	501
Carbon Black. Control Tests of Uniformity of	598
-Rubber Mixtures. Flocculation of Pigment in	575
Colloidal	187
Cements. Properties of Rubber	142
Chemistry of Soft Rubber Vulcanization. Reversion and Nonreversion in Low-Sulfur Compounds	680
Coagulation of Latex of Hevea Brasiliensis	60
Coagulation of Latices by Polar-Nonpolar Liquids	87
Colloidal and Chemical Investigation of Different Brands of Latex; Natural Latex, Jatex, Revertex, Revertex-T, and Revultex	630
Carbon. pH Properties of	187
Clay. Studies of System Latex-	433
Structure of Rubber in Solution. Effects of Precipitants	663
Comparative Viscometric Studies of Solutions of Crepe Rubber and of Buna	372
Components of Hevea Latex. Part II. Seasonal Variations in the Composition of Typical Seedling Latex	445
Part III. Analyses of Plantation Rubber and of Creamed Latices	452
Part IV. Effect of Ammoniation on Latex	455
Composition and Structure of Hevea Latex	394
Compression Tests on Vulcanized Rubber	561
Concentration of Latex by Creaming	75
Conductivity of Rubber. Thermal	359
Contribution to the Early History of India Rubber	1
Contribution to the History of Latex	482
Contributions to the Analysis of Rubber. III. Determination of Copper in Raw Rubber, in Mixtures, and in Fillers	706
Control Tests of Uniformity in the Manufacture of Carbon Black	598
Coöperation in the Rubber Industry. Research	263
Copper in Raw Rubber	706
Creamed Latices. Analyses of Plantation Rubber and of	452
Creaming. Concentration of Latex by	75
Creaming of Hevea Latex by Colloids	608
Crystallization of Rubber. Influence of Temperature on	348
Depolymerization of Natural Rubber by Quinones and Related Compounds	47
Deposition of Rubber on to Textile Fibers	545
Detection and Analysis of Organic Accelerators	531
of Accelerators. Rapid	210
Dithiocarbamate Accelerators in Vulcanized Rubber	533
Guanidine Accelerators in Vulcanized Rubber	531
Thiuram Accelerators in Vulcanized Rubber	535
Determination of Copper in Raw Rubber, Mixtures, and Fillers	706
Resistance of Vulcanized Rubber to Tearing	689
Rubber. A New Method for the Direct	438
Difficulties in the Thorough Impregnation of Textiles with Latex	538
Dithiocarbamate Accelerators in Vulcanized Rubber	533
Ebonite. Impact Test for	224
Behavior towards Organic Liquids	147
Effect of Organic Accelerators on the Temperature Coefficient of Vulcanization	101
Elasticity of Rubber. Kinetic Theory of	644
Electric Currents, High Frequency in Latex Industry	570
Enhanced Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds	47
Estimation of the Stability of Rubber Solutions	558
Extraction of Water-Soluble Accelerators in Water Cure	591

	Page
Falling-Weight Impact Test for Ebonite	224
Ficus Elastica Latex, Stability of	624
Fillers, Determination of Copper in	706
Flocculation of Pigment in Carbon Black–Rubber Mixtures	575
Fluorescence of Vulcanization	310
Fusion Curves of Rubber and Gutta-Percha	658
Gel and Total Rubber, Sol. X-ray Diffraction Patterns of	32
Gough-Joule Effect in Vulcanizates	508
Guanidine Accelerators in Vulcanized Rubber. Detection of	531
Gutta-Percha. Fusion Curves of Rubber and	658
Highly Reactive Sulfur or the Reaction of Ammonia and Sulfur Chloride in Rubber Solutions	92
History of India Rubber. Contribution to the Early	1
History of Latex	482
History of Rubber. Franz Carl Achard's "Experiments on Elastic Resin"	653
Hydratant Acid. Separation of, from Latex	60
Impact Test for Ebonite	224
Impregnation of Textiles with Latex. Difficulties in Thorough	538
Influence of the Crystallographic Transformation of Sulfur on the Course of Vulcanization	317
the Temperature on the Crystallization of Rubber	348
Vulcanization on Oxidizability in Relation to Aging. A Preliminary Study	282
Investigation of the Thermal Conductivity of Rubber	359
Isomerization of Rubber	350
Jatex. Colloidal and Chemical Investigation of	630
Joule Effect in Vulcanizates. Gough-	508
Kinetic Theory of the Elasticity of Rubber	644
Kinetics of Coagulation of the Latex of Hevea Brasiliensis and the Separation of the Hydratant Acid	60
Latex. Colloidal and Chemical Investigation of Different Brands of	630
-Colloidal Clay. Studies of the System	433
Components of Hevea	445
Composition and Structure of Hevea	394
Compounds. Preparation and Testing of	716
Concentration by Creaming	75
Creaming by Colloids of Hevea	608
Effect of Ammoniation on	455
History of	482
Impregnation of Textiles with Latex	538
Industry. Some Applications of High-Frequency Electric Currents to the	570
Preparation and Determination of Quality	459
Proteins in Preserved Hevea	601
Some Properties of Rubber	479
Stability of Ficus Elastica	624
Ultraviolet Microscopy of Hevea Rubber	405
Latices. Coagulation by Polar-Nonpolar Liquids	87
Creamed. Analyses of	452
Low-Sulfur Compounds. Reversion and Nonreversion	680
Manometer for Measuring the Oxidizability of Rubber	268
Marking of Uncured Rubber Mixes	441
Mechanism of Action of Accelerators of Vulcanization. Derivatives of Mercaptobenzothiazole. II. Transformation of Mercaptobenzothiazyl Sulfide	97
Rubber Vulcanization with Sulfur	107
Mercaptobenzothiazole. Derivatives of	97
Mercaptobenzothiazyl Sulfide. Transformation of	97
meta-Dinitrobenzene. Vulcanization of Rubber with	131, 319
Metallic Oxides. Activating Influence of	331
Microscope. Some Applications to Rubber Technique	197
Microscopy of Hevea Rubber Latex. Ultraviolet	405
Natural and Synthetic Rubber. XVIII. The Protein from Natural Rubber and Its Amino Acid Constituents	5
Neoprene, Water Resistance of	383
New Method for the Direct Determination of Rubber. A Preliminary Communication	438
New Transformation Product of Rubber	661
Observations on the Viscosity of Rubber Solutions	676
Oppanol. Rubber-like Behavior of an Artificial Substance	687
Oxidation Products of Rubber: Rubbone	523
Oxidizability. Influence of Vulcanization on	282
of Rubber. A Manometer for Measuring the	268
Oxygen Pressure Aging. Improved Equipment	722
Ozonides, Various Rubber	7
Packing of Rubber. Improved	439
Particle Size. Pigment	585
Permeability of Organic Polysulfide Resins to Hydrogen	163
pH Properties of Colloidal Carbon	187
Pigment Particle Size and Surface. Processing Characteristics of Rubber Compounds as Affected by	585

Page

Plant. Study of Formation of Rubber in the ... 57
Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds. 47
of Butadiene and the Production of Artificial Rubber ... 501
Polysulfide Resins. Permeability of Organic ... 163
Precipitants. Effects of, on Colloidal Structure of Rubber in Solution ... 663
Preparation and Testing of Latex Compounds ... 716
of Latex and Determination of Quality ... 459
Processing Characteristics of Rubber Compounds as Affected by Pigment Particle Size and Surface ... 585
Properties of Rubber Cements ... 142
Protein from Natural Rubber ... 5
Proteins in Preserved Hevea Latex ... 601
Puncture Resistance. Apparatus for Evaluating ... 740
Purification and Concentration of Rubber Latex with Special Reference to Dialysis ... 423

Quinones and Related Compounds. Enhanced Polymerization and Depolymerization of Rubber by ... 47

Rapid Detection of Accelerators ... 210
Raw Rubber, Behavior of, when Stretched Isothermally ... 647
Determination of Copper in ... 706
Research Coöperation in the Rubber Industry ... 263
Resins. Polysulfide, Permeability to Hydrogen of Organic ... 163
Reversion and Nonreversion in Low-Sulfur Compounds ... 680
Revertex, Colloidal and Chemical Investigation of ... 630
Revertex-T. Colloidal and Chemical Investigation of ... 630
Revultex. Colloidal and Chemical Investigation of ... 630
Rubber. XVIII. Various Rubber Ozonides and the Problem of the Existence of the Primary Ozonides of Harries ... 7
-like Behavior of an Artificial Substance (Oppanol) when Irradiated with X-rays ... 687
Rubbone. Oxidation Products of Rubber ... 523

Sol, Gel, and Total Rubber. X-ray Diffraction Patterns of ... 32
Solutions. Highly Reactive Sulfur ... 92
of Crepe Rubber and of Buna. Comparative Viscometric Studies of ... 372
Stability of Rubber ... 558
Viscosity of Rubber ... 676
Some Applications of High-Frequency Electric Currents to the Latex Industry ... 570
The Microscope to Rubber Technique ... 197
Some Properties of Rubber Latex ... 479
Sorption of Rubber ... 485
Stability of Ficus Elastica Latex ... 624
Rubber Solutions. Estimation of ... 558
Stretched Rubber. Structure of ... 510
X-ray Study of ... 352
Structure, Colloidal, of Rubber in Solution ... 663
of Hevea Latex, Composition and ... 405
Stretched Rubber ... 510
Studies of Organic Accelerators. XVI. Part 4. Detection and Analysis of Organic Accelerators. Detection of Guanidine Accelerators in Vulcanized Rubber ... 531
XVIII. Part 6. Detection of Dithiocarbamate Accelerators in Vulcanized Rubber ... 533
XIX. Part 7. Detection of Thiuram Accelerators in Vulcanized Rubber ... 535
Studies of the System Latex-Colloidal Clay ... 433
Study of the Formation of Rubber in the Plant ... 57
Sulfur in Rubber Solutions, Highly Reactive ... 92
Influence of Crystallographic Transformation of ... 317
Synthetic Rubber. Natural and ... 5

Tearing. Determination of Resistance of Vulcanized Rubber to ... 689
Temperature Coefficient of Vulcanization. Effect of Organic Accelerators on the ... 101
Influence on Crystallization of Rubber ... 331
Tension Tests with Flat (Straight) Test-Specimens ... 214
Testing of Latex Compounds. Preparation and ... 716
Textile Fibers. Deposition of Rubber on to ... 545
Textiles. Impregnation with Latex ... 538
Thermal Conductivity of Rubber ... 359
Thiuram Accelerators in Vulcanized Rubber. Detection of ... 535
Total Rubber, Sol, Gel, and. X-ray Diffraction Patterns of ... 32
Transformation Product of Rubber. A New ... 661

Ultraviolet Microscopy of Hevea Rubber Latex ... 405
Uniformity in Manufacture of Carbon Black. Control Tests of ... 598

Viscometric Studies of Solutions of Crepe Rubber and of Buna ... 372
Viscosity of Rubber Solutions ... 676
Vulcanization. Activating Influence of Metallic Oxides on ... 331
Chemistry of Soft Rubber ... 680
Fluorescence of ... 310
Influence of Crystallographic Transformation of Sulfur on Course of ... 317
Influence on Oxidizability in Relation to Aging ... 282
of Rubber in the Presence of meta-Dinitrobenzene ... 131, 319
with Sulfur, Mechanism of ... 107

Water Resistance of Neoprene ... 383

X-ray Diffraction Patterns of Sol, Gel, and Total Rubber when Stretched, and when Crystallized by Freezing and from Solutions ... 32
X-rays, Rubber-like Behavior of Artificial Substance (Oppanol) when Irradiated with ... 687

NORMAL —
PROCESSED —
CONCENTRATED

HEVEATEX

RUBBER
LATEX

Always In Stock For Immediate Delivery

HEVEATEX
CORPORATION
78 GOODYEAR AVE.
MELROSE, MASS.
U.S.A.

ANTIMONY
SULPHIDE—

Regular Grades
for Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

◆

Rare Metal Products Co.
Belleville, New Jersey

Business Credentials

Quality products are the finest credentials any firm can show as evidence of reliability. They pave the way for doing business on a lasting foundation of trust. May we present our credentials in the form of samples to prove how efficiently and dependably we can meet your requirements for these and other products?

- **CARBON BLACK**
- **HYDRO CARBON**
- **STEARITE**

WITCO

WISHNICK-TUMPEER, INC.
Manufacturers and Importers

New York, 295 Madison Avenue • Boston, 141 Milk Street • Chicago, Tribune Tower • Cleveland, 616 St. Clair Ave., N. E. • Harold Wilson & Witco, Ltd., 6 Portman Mansions, Baker Street, London, W 1, England • Witco Affiliates: • Witco Oil & Gas Company • The Pioneer Asphalt Company • • Panhandle Carbon Company

BUY DIRECT AND PROFIT DIRECTLY

TESTED

(Always Uniform!)

AZO

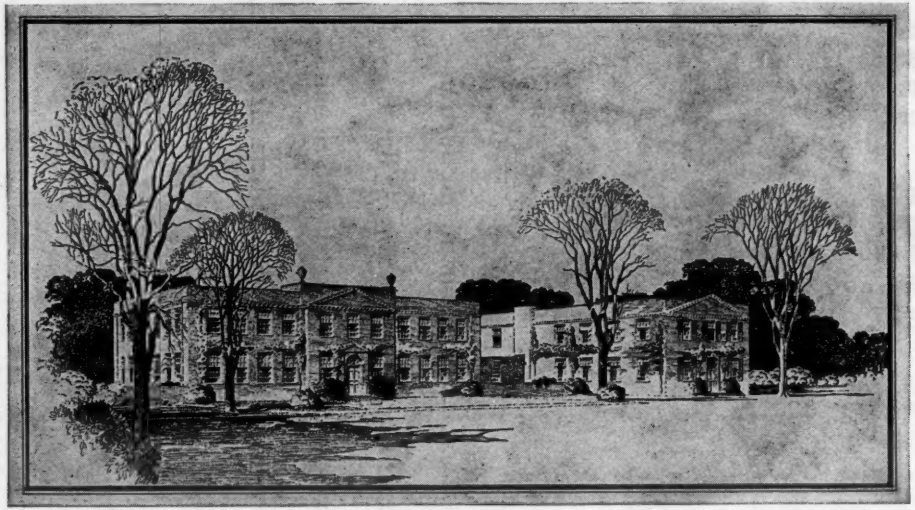
ZINC OXIDES

AMERICAN ZINC SALES CO.

DISTRIBUTORS FOR

AMERICAN ZINC, LEAD & SMELTING CO.

COLUMBUS, O. P. O. Box 327 | CHICAGO—77 W. Washington St. | ST. LOUIS—943 Paul Brown Bldg. | NEW YORK Graybar Bldg.



In this laboratory we try to learn how our materials may be used to best advantage by our customers. Your cooperation is helpful and invited; you are welcome to visit our laboratory, discuss your problems, and to work on them there if you care to do so.

R. T. VANDERBILT CO.

230 Park Avenue, New York, N. Y.

WE LIKE THE TOUGH ONES

Your requirements for Zinc Oxide in the production of rubber may be particularly exacting. But the tougher your requirements may be relative to chemical purity, uniformity, cleanliness and particle size, one of the grades of St. Joe Zinc Oxide will solve your problem quickly and economically.

Produced by Our Patented Electro Thermic Process

ST. JOSEPH LEAD COMPANY

250 PARK AVE., NEW YORK ELdorado 5-3200

RESEARCH LABORATORY, JOSEPH WYLIE MEMORIAL, MONACA, PA.

Now Available

ANNUAL BIBLIOGRAPHY OF RUBBER LITERATURE FOR 1937

Compiled by DR. D. E. CABLE

Third in the series of annual bibliographies, this latest edition lists all articles on subjects of special interest to rubber chemists, technologists, engineers, etc., which appeared in rubber and other journals throughout the world during 1937. As in the two previous editions (for 1935 and 1936, respectively), it has extensive subject and author indexes.

●

128 Pages—6 x 9 in.

PRICE: $1.00 (Paper-Bound)
2.00 (Cloth-Bound)

THE RUBBER AGE

250 West 57th Street New York City

CATALPO

Justifies its use always for

COMPOUNDING

—Carcasses, Tires

—Inner Tubes

—Insulated Wire

—Mechanical Goods and Latex

Write our Technical Service Dept.
33 Rector St., New York City

MOORE AND MUNGER

212 PARK AVE.
PLAINFIELD, N. J.

DOMINANT IN THE RUBBER INDUSTRY SINCE 1889

FOR NEARLY A HALF CENTURY

INDIA RUBBER WORLD

Has kept the industry fully informed on technical questions and developments as well as new processes, equipment and products, publishing papers by trade authorities and news from correspondents throughout the world.

Edited by technical men who have had long practical experience in rubber compounding and production.

THE RECOGNIZED AUTHORITY

PROOF { FAR LARGER CIRCULATION AND 150% *MORE* ADVERTISING THAN ANY OTHER PUBLICATION IN THE FIELD.

$3.00 PER YEAR IN U. S.—$3.50 IN CANADA—
$4.00 ELSEWHERE

COMPOUNDING INGREDIENTS
FOR RUBBER

A comprehensive presentation of outstanding ingredients, their composition, physical state, properties, applications and functions.
Price $2.50. Postpaid in U. S. A. Elsewhere, $2.75.

ANNALS OF RUBBER

A chronological record of the important events in the history of rubber from 1519 to 1936.

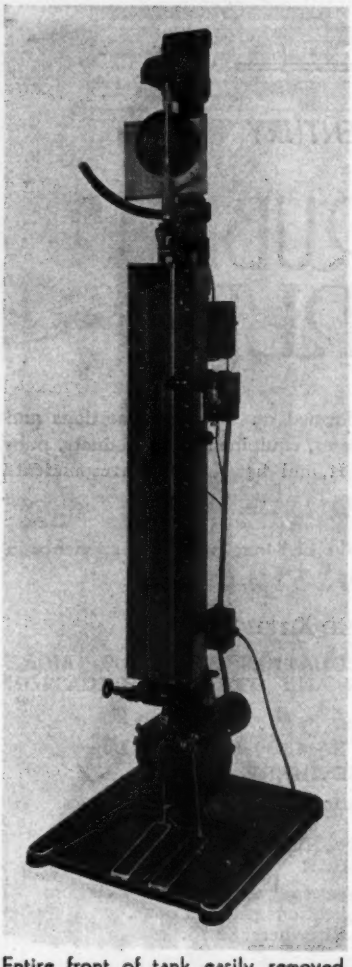
20 pages—paper bound—50c per copy.

INDIA RUBBER WORLD

420 LEXINGTON AVE. NEW YORK, N. Y.

SCOTT Model LP *Rubber Tester*

With Controlled Temperature Water Bath



Entire front of tank easily removed permitting the use of this machine in the conventional manner.

▲▼▲

Efficient

Accurate

Motor Driven

Simple to Operate

Instantaneous Reverse

Spark Type Recorder

▲▼▲

HENRY L. SCOTT CO.

Box 963 **Providence, R. I.**

"NEOPHAX" VULCANIZED VEGETABLE OIL

Trade Mark Reg. U. S. Pat. Office

FOR USE WITH NEOPRENE

The Stamford Rubber Supply Co.

at Stamford, Conn., U. S. A., Since 1900

The C. P. HALL Company

CHEMICALS

for the RUBBER TRADE

Accelerators Antioxidants
Fillers Pigments Fluxes

Akron Los Angeles

RUBBER CHEMICALS

A DIVERSIFIED LINE

For All Branches of the Rubber Industry

Naugatuck Chemical has pioneered in the development, manufacture, and marketing of rubber chemicals since the inception of modern rubber compounding and today offers a complete line of accelerators, antioxidants, and of special products, as odor coordinators, plasticisers, rubber labels and rubber inks. All Naugatuck Products are of established value. This company, because of its accumulated knowledge, plus its reputation for quality products, solicits your special rubber compounding problems and offers you the technical assistance of its large and active research laboratory.

ACCELERATORS

Beutene
B-J-F
Crylene
Di-Esterex-N
Heptene Base
Monex
O-N-V
Ovac
O-X-A-F
Pentex
Trimene Base
Trimene
Z-M-L
C-P-B
D-B-A
Z-B-X

ANTIOXIDANTS

Albasan
B-X-A
B-L-E
B-L-E Powder
M-U-F
V-G-B

SPECIAL PRODUCTS

A-X-F
Laurex
Sunproof
Tonox D
U-T-B
A-F-B
Amora

Naugatuck Chemical

DIVISION OF UNITED STATES RUBBER PRODUCTS, INC.

1790 BROADWAY NEW YORK, N. Y.

CALCENE

(Reenforcing Calcium Carbonate)

Gives that desired processability to light mechanical goods, while improving tensile, tear and resistance to abrasion.

The Columbia Alkali Corporation
Barberton, Ohio.

COLORS for RUBBER

RED IRON OXIDES
GREEN CHROMIUM OXIDES
GREEN CHROMIUM HYDROXIDES

Reinforcing Inerts
and
Fillers

C. K. WILLIAMS & CO.

EASTON, PENNA.

CHANGE OF ADDRESS

after

OCTOBER 14, 1938

For more efficient service

The main office of

THE CARTER BELL MFG. CO.

Will be moved from

New York City to its plant at

SPRINGFIELD, NEW JERSEY

To the Rubber Industry!

This Journal is supported by advertising from leading suppliers to the industry. More advertising will permit the publication of a greater number of important technical papers on rubber which will make RUBBER CHEMISTRY AND TECHNOLOGY even more valuable as a convenient reference of "Rubberana."

Specify materials from suppliers listed on opposite page. Urge other suppliers to advertise in

RUBBER CHEMISTRY AND TECHNOLOGY

Advertising rates and information about available locations may be obtained from S. G. Byam, Advertising Manager, Rubber Chemistry and Technology, care of Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware.

GASTEX QUARTERLY SUMMARY

GASTEX PELLETEX

VOL. 2 OCTOBER • 1938 No. 4

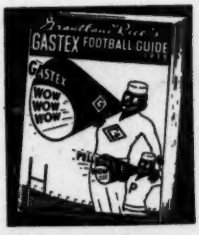
GASTEX COMBINATIONS . . .

Our new Laboratory Report No. 142 shows that a compound containing equal loadings of GASTEX and channel black combines desirable low heat build-up from the GASTEX with satisfactory tensile and abrasion properties from the channel black. This important report of an impartial study made with various combinations of GASTEX and channel black gives full details on flexometer temperatures, normal and aged tensiles at various cures for the following stocks:

	1k1	1k2	1k4	1k6	1k8
Smoked Sheets	100	100	100	100	100
ZnO	5	5	5	5	5
Sulfur	3	3	3	3	3
Stearic Acid	3	3	3	3	3
Pine Tar	2	2	2	2	2
Age Resistor	1	1	1	1	1
Channel Black	50	37.5	25.0	12.5	0
Gastex	0	12.5	25.0	37.5	50.
M.B.T.	1	.85	.70	.55	.40

Cured 20, 30, 45, 60, 90 and 120 min. at 274 degrees F.

Send for a copy of Report No. 142.



GASTEX Football Schedules

Send for your copy of Grantland Rice's GASTEX Football Guide for 1938 containing complete football schedules of leading teams, other football information and important data on GASTEX, the special process black, and PELLETEX, the pellet form of GASTEX.

Is your name on our mailing list?

GENERAL ATLAS CARBON COMPANY

SIXTY WALL STREET GASTEX TRADE MARK NEW YORK, N. Y.

Sales Representatives: HERRON & MEYER, INC.

NEW YORK AKRON CHICAGO

GAS . . . .

FOR HOUSES OF FLAME

There are 366 burner houses, such as these shown here, in Continental's carbon black plant at Sunray, Texas. In each, hundreds of flames are burning day and night, producing carbon black for the growing needs of industry. These houses are under the constant observation of men patrolling up and down the line. The man in this picture is inspecting the appearance of the flames in one of them. Gas is supplied through the big pipe which circles the entire plant in a huge loop. This assures a more uniform distribution of gas to all houses —just one of the many factors that contribute to the uniformity of Continental Carbon Black, and to the confidence with which it may be used in your formulas.

Continental

CARBON COMPANY

295 Madison Avenue, New York, N. Y.

Advertisers in this issue

American Zinc Sales Company

Cabot, Godfrey L., Inc.

Carter Bell Manufacturing Company

Columbia Alkali Corporation

Continental Carbon Company

Du Pont Rubber Chemicals Division

General Atlas Carbon Company

Hall, C. P., Company, The

Heveatex Corporation

India Rubber World

Moore & Munger

Naugatuck Chemical Division (U. S. Rubber Products, Inc.)

New Jersey Zinc Company

Pequanoc Rubber Company

Rare Metal Products Company

Rubber Age

Rubber Service Laboratories Division (Monsanto Chemical Co.)

St. Joseph Lead Company

Scott, Henry L., Company

Stamford Rubber Supply Company

Thiokol Corporation

Thompson, Weinman & Co., Inc.

United Carbon Company

Vanderbilt, R. T., Co., Inc.

Williams, C. K., & Company

Wishnick-Tumpeer, Inc.